INCREASED BIOGAS PRODUCTION BY ANAEROBIC CO-DIGESTION OF WASTEWATER SLUDGE WITH FRUIT AND VEGETABLE WASTE, AND BY SLUDGE PRE-TREATMENT

By

Nathan D. Park

B.Sc., University of Northern British Columbia, 2008

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE
IN
NATURAL RESOURCES AND ENVIRONMENTAL STUDIES
(ENVIRONMENTAL SCIENCE)

UNIVERSITY OF NORTHERN BRITISH COLUMBIA

January 2012

Library and Archives Canada

Published Heritage Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et Archives Canada

Direction du Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence
ISBN: 978-0-494-87588-9

Our file Notre référence
ISBN: 978-0-494-87588-9

Abstract

Full scale anaerobic co-digestion of fruit and vegetable waste (FVW) and municipal wastewater primary sludge significantly increased biogas production. Digester operation remained stable. Undigested FVW was visible in dewatered sludge suggesting that FVW should be added to the first stage digester to prevent short-circuiting and increase the hydraulic retention time (HRT) of the FVW. Batch lab results confirmed that co-digestate addition to first stage sludge (FSS) is preferred to second stage sludge (SSS). FSS produced significantly more methane (514 ± 57 L CH_4 $kgVS^{-1}_{added}$) than SSS (392 ± 16 L CH_4 $kgVS^{-1}_{added}$). In a related study, combined alkaline and ultrasonic pre-treatment of thermomechanical pulp mill sludge (PMS) significantly increased the soluble TS, VS, and COD of the PMS over non-treated sludge. Pre-treatment did not significantly improve biogas production over 28 d, but did increase VS reduction, and the initial rate of methane production. Overall, biogas production from PMS was inconsistent.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICIES

ACKNOWLEDGEMENT

Firstly, and most importantly, I would like to thank Dr. Ron Thring. I chose Dr. Thring as my supervisor due to a small gesture he made acknowledging an undergraduate project I presented in his class. At the time I did not know how important of a decision this was, but I am glad I made such an excellent choice. I appreciate his understanding, advice, direction, and independent guidance. He was always looking out for my best interest. I am grateful for his patience as I jump from topic to topic during a conversation. I am especially glad that he is always pushing me to do things outside of my comfort zone and ensuring that I get the most out of my degree as possible in the least amount of time. Thank you.

I am also very thankful for the help that was given to me by all of my committee members. I appreciate the extra effort Dr. Mike Rutherford put in working on our side projects and for always being welcoming when I interrupted him. I would also like to thank Dr. Steve Helle for always having a question that I didn't know the answer to. These questions tended to be crucial. Thank you too to Mr. Randy Garton. His years of direct experience in the wastewater treatment process provided a wealth of knowledge. I appreciate him allowing me to mess with his wastewater treatment plant.

Thank you to all of my friends: Jordan Keim, Adam Middleton, Bobby Chavarie, Harpuneet Singh and Mateusz Partyka for always reminding me that I can do it tomorrow. Some things are more important than work.

Lastly, I would like to thank Amy for being the motivation to better myself, for always being positive and helpful, listening to me, and always believing in me. I'm sorry I was never home for dinner.

CHAPTER 1. Introduction

1.1 A short history of anaerobic digestion

Anaerobic digestion (AD) has been used by humans to produce energy as far back as the 10th century. It is believed that the ancient Assyrians used methane gas produced from animal wastes to heat bath water (Stepan, 2008). Lessandro Volta, in the 18th century, was the first scientist to report that gas collected from aquatic sediments was combustible (McCarty, 2001). He concluded that the organic matter contained in aquatic sediments was producing "combustible air" (McCarty, 2001). Faraday, Dalton, Henry, and Davy continued to work with this "combustible air" until in 1821 Amedeo Avogadro concluded that the chemical structure of the flammable gas was CH_4 (Deublin and Steinhauser, 2008). One of the first practical applications of anaerobic digestion was applied to wastewater in 1860 (McCarty, 2001). The "Mouras Automatic Scavenger", invented by M.L. Mouras, was an airtight tank that was used for the stabilization of sewage. The invention was reported in the French Journal *Cosmos* and claimed to be the "complete solution to the problem which for centuries had been an insolent menace hurled in the face of humanity" (Moigno and Mouras, 1882). In 1895, methane gas produced from waste was being utilized as an energy source in Exeter, England. The methane gas produced from treatment of wastewater was used for heating and lighting at the sewage disposal plant (McCarty, 2001). Around the same time at a leper colony in Bombay, India, sewage disposal tanks were being fitted with gas collectors in order to store the methane produced for use in engines (AEBIOM, 2010).

In the 20th century, research and development of AD was concerned with wastewater stabilization and sludge solids reduction more than energy production.

Around 1905, Imhoff and Travis each designed a two stage sludge digestion system (that bears their names) for the stabilization of solids collected from wastewater (McCarty, 2001). From 1930-1950 the optimization of the AD process was investigated by studying parameters such as temperature, pH, mixing and retention times. In the 1970's more complex AD systems were invented in order to increase waste stabilization and methane gas production. These systems included; the anaerobic contact process, the anaerobic filter, and the up flow anaerobic sludge blanket reactor. A short timeline summarizing the main events in the development of anaerobic digestion is presented in Figure 1.

Although AD has been in use for well over 100 years for the treatment of wastewater sludges, its potential for energy production is only now being fully recognized. Concerns over fossil fuel reserves, energy security, and anthropogenic climate change have sparked interest in the use of AD to produce renewable energy from wastes. Various agricultural, municipal, and industrial wastes have been successfully processed by anaerobic digestion on large scales (Alatriste-Mondragon et al., 2006). European nations have become a leader in this technology with over 6000 AD facilities currently operating within the European Union (AEBIOM, 2010). Canada by comparison, with its abundance of cheap fossil fuels, and lack of government legislation pertaining to waste disposal, has approximately 17 digesters in operation (IEA, 2010). However, Canada is a budding market with over 34 new anaerobic digestion plants expected to be complete by 2012 (IEA, 2010).

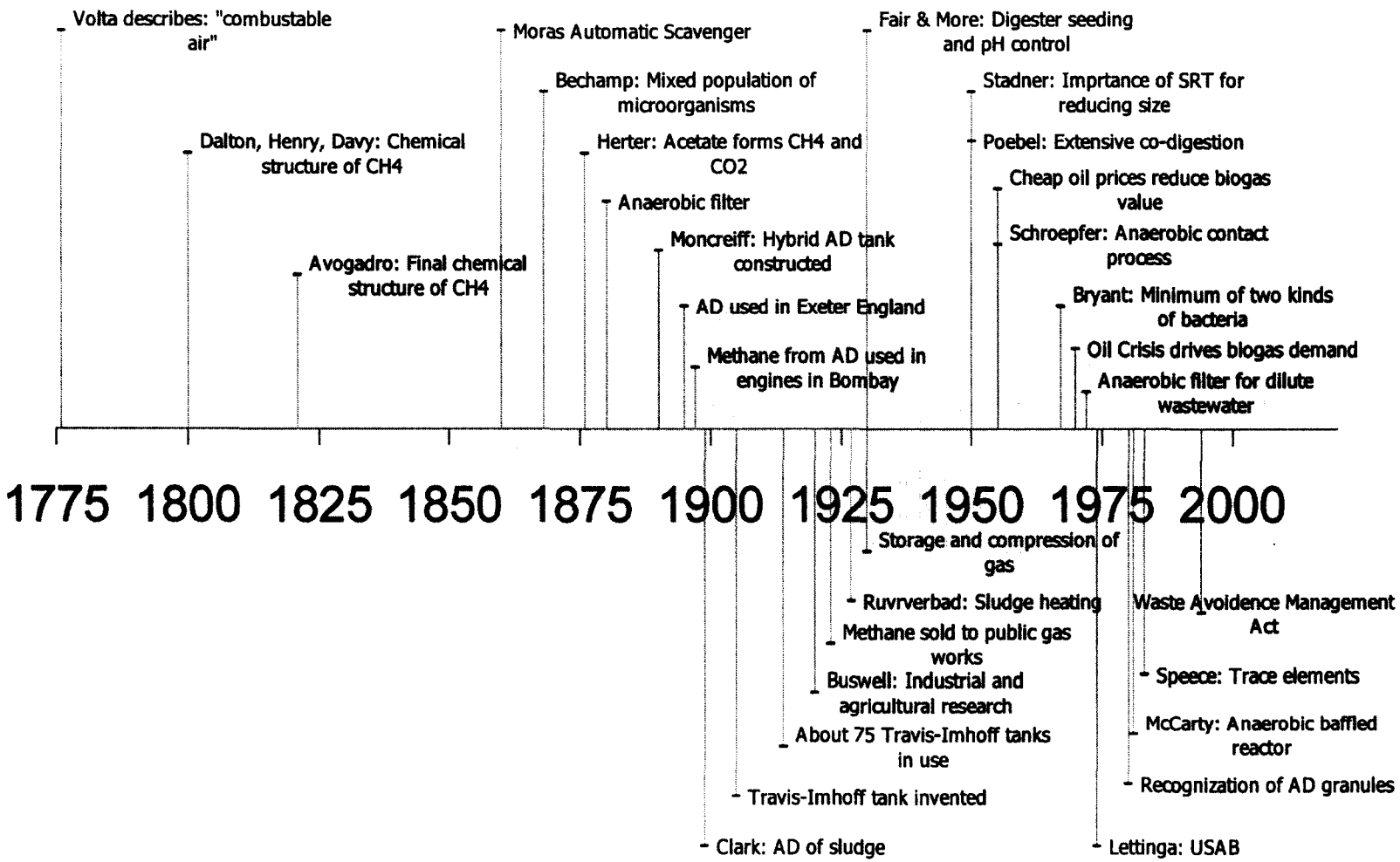

Figure 1.0 The history of anaerobic digestion (Deublin and Steinhauser, 2008; Khanal, 2008; McCarty, 2001)

1.2 The biology of anaerobic digestion

Anaerobic digestion is the biological process by which organic matter is broken down into methane and carbon dioxide in an anoxic environment. It is a natural process that occurs in mud, ocean sediments, and the guts of ruminants. AD is an extremely complex, sequential, synergistic process, carried out in cooperation by Archaea, bacteria, fungi, yeast, and protozoa. A typical anaerobic digester can contain over 120 different species of bacteria having a density greater than 10^{16} bacterial cells mL^{-1} (Gerardi, 2003). The process can be divided into four sequential stages each having its own flora of organisms. The four stages are described in detail below.

1.2.1 Hydrolysis

The first step of the AD process is termed hydrolysis. Large, insoluble polymers are broken down by enzymes such as lipases, cellulases, and proteases into smaller more soluble monomers. Solubilization is necessary in order for the molecules to enter the bacterial cell and therefore the majority of the enzymes used are released extracellularly. The process is very complex with bacteria, fungi, and protozoa all contributing. The various rates of breakdown for large polymers are summarized in Table 1.0. When digesting waste streams made up of particulate matter, or complex materials that are difficult to degrade, hydrolysis is considered the rate limiting step of the methane forming process (Jeihanipour et al., 2011; Noike et al., 1985).

Table 1.0 Time frame for the hydrolysis of various polymers to their respective monomers (Deublin and Steinhauser, 2008).

Polymer		Monomer	Timeframe
Carbohydrates	→	Sugars	Hours
Fats	→	Fatty acids, Glycerine	Days
Proteins	→	Amino acids	Days
Lignocellulosic Compounds	→	Sugars	Slowly/Incompletely

1.2.2 Acidogenesis

The next step in the anaerobic digestion process is the conversion of the soluble monomers formed by the hydrolysis of complex molecules into short chain organic acids (volatile fatty acids), alcohols, carbon dioxide, and hydrogen. This phase is termed acidogenesis. As seen in Table 1.1, these short chain acids and alcohols are mostly less than five carbon atoms in length (Deublin and Steinhauser, 2008).

Table 1.1 Major acids and alcohols produced during acidogenesis (Gerardi, 2003).

Name	Formula
Acetate	CH_3COOH
Butanol	$CH_3(CH_2)_2CH_2OH$
Butyrate	$CH_3(CH_2)_2CH_2COOH$
Caproic acid	$CH_3(CH_2)_4COOH$
Formate	$HCOOH$
Ethanol	CH_3CH_2OH
Lactate	$CH_3CHOHCOOH$
Methanol	CH_3OH
Propanol	$CH_3CH_2CH_2OH$
Propionate	CH_3CH_2COOH
Succinate	$HOOCCH_2CH_2COOH$

Many of the bacteria involved in hydrolysis are also involved in acidogenesis. Therefore, the first two steps of the AD process are sometimes combined and termed, "anaerobic fermentation". Bacteria involved in this step have quick growth rates compared to

Methanogens and are much less sensitive to environmental conditions such as temperature, pH, and inhibiting compounds (Ahring et al., 2001).

1.2.3 Acetogenesis

Acetogenesis is the process by which the volatile fatty acids (VFA's) and alcohols produced by the acidogenic bacteria are converted to acetate and hydrogen.

Short chain acids + alcohols + $H_2O \rightarrow$ Acetate + $H^+ + H_2$ (ΔG= + 9.6-76.1 kJ)

The oxidation of the short chain acids is not thermodynamically favorable. Only when the partial pressure of H_2 is low will the reaction occur. The acetogenic organisms must therefore live symbiotically with the methanogenic bacteria that consume H_2 in order for the reaction to take place. This phenomenon is known as "interspecies hydrogen transfer", or syntropic interaction (Deublin and Steinhauser, 2008; Amani et al., 2010). The second group of organisms present in this phase is the homoacetogens. Homoacetogens reduce H_2 and CO_2 to acetate.

$$2CO_2 + 4H_2 \rightarrow CH_3COOH + H_2O$$

1.2.4 Methanogenesis

The methanogenic class of organisms is not made up of bacteria at all, but are organisms from the kingdom Archaea. Archaea are descendents of some of the most primitive life on earth when the atmosphere was much reduced (Novaes, 1986). Archaea are distinguished from bacteria by their lack of peptidoglycan, membrane lipids, and distinct RNA (Khanal, 2008). There are three main groups of methanogenic organisms that are used for the formation of methane and they are distinguished by which substrate they utilize.

Table 1.2 Methanogenic species type differentiated by substrate utilization. (Deublin and Steinhauser, 2008).

Type	Example Reaction
CO_2 Type	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$
Methyl Type	$CH_3OH + H_2 \rightarrow CH_4 + H_2O$
Acetate type	$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3$

The majority of methane, about 70%, is produced from the acetate pathway whereas 30% is generated from the reduction of CO_2 (Khanal, 2008; Deublin and Steinhauser, 2008). The CO_2 pathway is favored energetically, but limited due to the amount of hydrogen present in the digester (Amani et al., 2010). If sulphate is present in the waste, a group of organisms called, "sulphur reducing bacteria (SRB)" compete for substrates and reduce sulphur to form hydrogen sulphide gas (Khanal, 2008). If nitrate is present, it will act as an electron acceptor and become reduced to nitrogen gas. Bacteria that reduce nitrogen are called, "nitrate-reducing bacteria (NRB)".

1.2.5 Biogas

Microbial action causes the reduction and stabilization of the wastewater sludge and produces biogas. The concentrations of different compounds in the biogas can vary greatly depending on the characteristics of the waste used in digestion. Some of the various components and their respective concentrations can be seen in Table 1.3.

Table 1.3 Components and potential impurities in biogas (Deublin and Steinhauser, 2008).

Component	Concentration	Origin
Methane	50- 75% (vol.)	Reduction of organic waste
Carbon Dioxide	25-50% (vol.)	Reduction of organic waste
Hydrogen sulphide	0-5% (vol.)	Reduction of sulphate by SRB
Ammonia	0-0.05% (vol.)	Reduction of N compounds, influent
Nitrogen	0-5% (vol.)	Reduction of nitrate by NRB, air
Water	1-5% (vol.)	Due to heating water
Siloxanes	0-50 mg m^{-3}	Degradation of cosmetics/detergents

Depending on the amount of methane present in the biogas it has an energy content of 6.0-6.5 kWh m^{-3} of biogas and the fuel equivalent of 0.6-0.65 L oil m^{-3} of biogas at STP (0°C, 1 atm) (Deublin and Steinhauser, 2008).

1.3 Parameters effecting anaerobic digestion

1.3.1 Temperature

Like any biological system AD is dependant of temperature. Even small temperature changes of ± 2° C can temporarily stunt biogas production (Chae et al., 2008). Methanogens are the most sensitive group of organisms to temperature changes. Hydrolysis and acidogenesis can occur over a much wider temperature range (Gerardi, 2003). There are three main temperature ranges that AD can be performed at (Table 1.4). Each temperature is preferred by a different array of methanogenic organisms. Mesophilic digestion is the most popular due to its lower energy requirement than thermophilic digestion, shorter retention time than psychrophilic digestion, and the larger variety mesophilic Methanogens. In general, more species of Methanogens prefer mesophilic temperatures (Deublin and Steinhauser, 2008; Gerardi, 2003).

Table 1.4 Common temperature ranges for methane forming bacteria.

Name	Temperature (°C)
Hyperthemophiles	> 65
Thermophilic	48-55
Mesophilic	35-40
Psychrophilic	5-15

Thermophilic digestion is beneficial when destruction of pathogens is necessary, or higher loading rates are required, however; it costs more to operate, it is more sensitive to temperature changes, and is more sensitive to toxic compounds. Psychrophilic digestion is most often performed in small scale sewage treatment units such a septic tanks (Gerardi, 2003). Large scale psychrophilic AD has advantages in colder climates, but research is very limited in the field (Lettinga et al., 2001).

1.3.2 pH/Alkalinity

The pH and alkalinity are crucial operating parameters of the anaerobic digestion process. The buffering systems that maintain a neutral pH in the digester occur naturally. Even slight changes in digester pH indicate imbalances in activity and are an early warning for digester failure. A drop in digester pH, and a rise in biogas CO_2 concentration, indicates a problem with methanogenesis. Methanogens are most sensitive to environmental factors and if their activity decreases the level of volatile acids in the digester can raise causing acidification and more subsequent inhibition. Optimum Methanogen productivity is achieved at a pH of 6.7-7.5 (Deublin and Steinhauser, 2008). Thus, digester pH should be maintained at a pH near 7.0. The main buffering reaction in the digester that controls the digester becoming too acidic is the carbon dioxide-bicarbonate-carbonate shift (Deublin and Steinhauser, 2008). For this reason, an

atmosphere of at least 30% carbon dioxide is required to maintain the buffering system (McCarty, 1964).

$$CO_2 \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + 2CO_3^{2-}$$

When the pH is low, due to an increase in volatile acids, more carbon dioxide is dissolved in the water. When the pH increases the carbon dioxide turns into carbonic acid and lowers the pH. The secondary buffering system that controls the digester becoming too basic is the ammonia-ammonium system (Deublin and Steinhauser, 2008).

$$NH_3 + H^+ \leftrightarrow NH_4^+$$

A digester system should maintain an alkalinity of 1000 to 5000 mg L^{-1} to maintain a stable pH and allow sufficient time to correct imbalances (McCarty, 1964). Often, the ratio of volatile acids to alkalinity is used to monitor the buffering capacity. A ratio of 0.1-0.25 is favorable, 0.3-0.4 signifies digester upset, and at a ratio higher than 0.8 methanogenesis will be disrupted (Kahnal, 2008). Some factors that can cause pH unbalance in the reactor are; change in temperature, change in organic loading, change in nature of waste, and the presence of toxic materials (McCarty, 1964). A digester experiencing an upset in pH can be returned to stable operation by (Deublin and Steinhauser, 2008):

- adding chemicals (lime, calcium hydroxide, sodium hydroxide)
- lowering digester loading rate
- dilution
- increasing hydraulic retention time (HRT)
- co-digesting substrate with high buffering capacity

1.3.3 Nutrients

Nutrient requirements for anaerobic digestion are relatively low compared to aerobic treatment since only approximately 10% of the organic matter is utilized for

biomass synthesis (Kahnal, 2008). It is generally accepted that the optimal C/N ratio of waste for anaerobic digestion is 16-25:1 (Deublin and Steinhauser, 2008; Yen and Brune, 2007; Wu et al., 2010; Ward et al., 2008). If the C/N ratio is too high the microbes will not have the required nitrogen for growth; if the C/N ratio is too low ammonia inhibition can occur. Co-digestion of substrates with low (manure, sewage sludge) carbon to nitrogen ratios with high (paper, vegetables) carbon to nitrogen ratios can help to maximize methane production (Yen and Brune, 2007; Wu et al., 2010; Alattriste-Mondgradon et al., 2006). Often, nitrogen and phosphorous can be added to nutrient deficient systems by the addition of urea, ammonia, or phosphoric acid (Kahnal, 2008). The phosphorous requirement of a digester is approximately 1/7-1/5 that of the nitrogen (Kahnal, 2008).

There are numerous micronutrients required by the anaerobic system. Ni, Co, Fe, S^{2-}, Se, W, Mg have all been shown to be required micronutrients for methane formation (Singh et al., 1999). Specifically, cobalt and nickel are essential components of vitamin B12 and factor F430 which produce methane (Gerardi, 2003). Micronutrients are generally high in municipal sewage sludge, but can be lacking in some industrial wastewater treatment scenarios. Elements must be in a soluble form in order to be absorbed by bacteria. Deficiencies in micronutrients are often mistaken as a form of toxicity (Gerardi, 2003).

1.3.4 Hydrogen partial pressure

Hydrogen-producing acetogenic bacteria and hydrogen-consuming Methanogens work together in a symbiotic relationship during anaerobic digestion. If the concentration of hydrogen is too high acetogenic bacteria will not produce hydrogen; if it is too low

Methanogens will not have enough hydrogen for methane production. The maximum partial pressure of hydrogen is dependant on the specific bacteria present as well as the substrate (Deublin and Steinhauser, 2008).

1.3.5 Oxidation-reduction potential

The oxidation-reduction potential, or redox potential, must be maintained around -200-350 mV (Khanal, 2008). It is for this reason that the concentration of oxidizing agents, such as oxygen, sulphate, and nitrates should be as low as possible in the digester (Deublin and Steinhauser, 2008).

1.3.6 Mixing

Proper mixing of the anaerobic digestion process is required to ensure that nutrients, substrates, enzymes, and bacteria are able to remain in contact. However, it should not be too vigorous as to disrupt the spatial symbiotic relationship between Acetogens and Methanogens (Deublin and Steinhauser, 2008). Also, mixing ensures a consistent sludge temperature throughout the reactor, that biogas is removed from solution, that floating/sinking sludge layers are combined, and that fresh substrate is inoculated with bacteria (Deublin and Steinhauser, 2008). Mixing should be complete, yet minimal, to maintain spatial relationships between organisms and to reduce energy requirements (Stroot et al., 2001; Gerardi, 2003). Most often mixing is achieved through gas recirculation, sludge heating recirculation, or propellers.

1.3.7 Organic loading rate, SRT, and HRT

Organic loading rate (OLR) is usually expressed in volatile solids (VS) m^{-3} d^{-1}. The greater the organic loading rate, the greater the biogas production. However, if digester feed rate is increased too quickly overproduction of VFA's can occur. Volatile

fatty acids will not be utilized due to the slow regeneration time of methanogenic bacteria (days to weeks) compared to the quick regeneration rate of acidogenic bacteria (hours). This imbalance can cause the digester pH to drop and inhibition of methanogenesis will occur. For this reason, the OLR of a digester must be increased slowly. The OLR of a digester can be increased until substrate feed is approximately 12% total solids. At this consistency, mixing and pumping become difficult, water content is too low for cell growth, and material transfer is retarded (Deublin and Steinhauser, 2008). With a very low OLR microbial populations are low, biogas production is low, and the process is uneconomical. Usually digesters are designed for loading rates of 3.2-7.2 kg VS m^{-3} d^{-1}, but due to the low solids content of most wastewaters 0.5-0.6 kg VS m^{-3} d^{-1} is more typical in a municipal setting (Gerardi, 2003).

The SRT, or solids retention time, is the average time that the bacteria stay in the digester. The HRT, or hydraulic retention time, is length of time that the sludge remains in the digester. The HRT is determined by the ease of degradation of the substrate. Easily digested substrates, like glucose and cellulose, require a short HRT. More difficult to degrade substrates, such as lignin and hemi-cellulose, require a longer HRT. The maximum OLR of a digester is determined by its SRT. The SRT is a measure of the digesters ability to maintain a certain biodegradation rate (Khanal, 2008). A high SRT means a higher population of bacteria inside the digester. A high SRT is favorable because it improves the rate of organics removal, provides resistance to toxicity, increases buffering capacity of the sludge, makes the digester less susceptible to shock loads, and reduces the required size of the digester (Khanal, 2008; Gerardi, 2003). A variety of anaerobic digestion processes have been devised to maintain high SRT's by

either recycling digested sludge, or maintaining biomass on a fixed bed to prevent washout.

1.4 Inhibition of anaerobic digestion

A variety of environmental factors can inhibit AD at any of the four stages. All stages of anaerobic digestion must proceed together. If one stage is inhibited substrates for the remaining stages will not be available. Methanogens are by far the most sensitive to inhibition. Various organic, inorganic, and environmental inhibitors of the anaerobic digestion process are described below.

1.4.1 Oxygen

Oxygen is not inhibitory to the acidogenic bacteria; however, it is to the methanogenic (Deublin and Steinhauser, 2008). Inhibition of methanogenic bacteria begins at oxygen concentration of 0.1 mg L^{-1} (Deublin and Steinhauser, 2008).

1.4.2 Light

Light severely inhibits methanogenesis (Deublin and Steinhauser, 2008).

1.4.3 Ammonia/ammonium

Ammonia is formed by the degradation of proteins and urea. Ammonia (inhibiting) forms ammonium ions (less inhibiting) in solution. Free ammonium is used a nitrogen source for the microorganisms and free ammonia is toxic (Gerardi, 2003).

$$NH_4^+ \leftrightarrow NH_3 + H^+$$

The ratio of ammonia to ammonium is pH dependant and increases with an increase in pH. A rise in temperature also shifts the equilibrium towards ammonia increasing inhibition. The concentrations at which ammonia is detrimental is shown in Table 1.5 (McCarty, 1964):

Table 1.5 The effect of free ammonia on anaerobic digestion.

Concentration (mg L^{-1})	Effect
50-200	Beneficial
200-1000	No effect
1500-3000	Inhibitory when pH is high
3000+	Toxic

Ammonia may inhibit biogas formation through inhibiting methane forming enzymes directly, or by direct diffusion into cells disrupting proton/potassium transport (Kayhanian, 1999). Two practical methods to mitigate ammonia inhibition include; dilution of digester contents with water and adjustment of feedstock C/N ratio using a high carbon substrate (Kayhanian, 1999).

1.4.4 Sulphur compounds

Sulphur compounds originate from amino acids (cysteine and methionine) in high protein waste streams, or they can be found in industrial wastes such as pulp mill wastewater due to chemical addition. Sulphur is often found in wastewater as sulphate and does not inhibit methanogenesis directly. There are two major groups of sulphur reducing bacteria that reduce sulphate to sulphide (Chen et al., 2008). SRB can disrupt anaerobic digestion in a number of ways. Firstly, SRB can compete with the organisms involved in anaerobic digestion for various substrates in the sludge (Chen et al., 2008). There is the possibility that they may become dominant in the digester because they require less energy and do no need a symbiotic relationship with other organisms in order to grow (Deublin and Steinhauser, 2008). Secondly, dissolved hydrogen sulphide that is indirectly produced by the SRB can be poisonous to cells at concentrations above 50 mg

L^{-1} (Deublin and Steinhauser, 2008). The mechanism of toxicity is not fully understood, but it is known to be pH dependant because hydrogen sulphide diffuses across membranes more easily than sulphide (Gerardi, 2003). Hydrogen sulphide and its various disassociated forms are shown below.

$$H_2S \leftrightarrow HS^- + H^+ \leftrightarrow S^{2-} + 2H^+$$

Thirdly, H_2S can inhibit anaerobic digestion indirectly by precipitating trace metals, such as Fe and Co, which are essential for methanogenic enzyme function (Deublin and Steinhauser, 2008). Sulphur inhibition can be overcome by acclimatization, by increasing the COD/sulphate ratio, by addition of metal salts to form precipitates, or by the addition of molybdate in order to inhibit sulphur consuming organisms (Delee et al., 1998).

1.4.5 VFA's

The short chain organic acids that are formed during acidogenesis are normally consumed by acetogentic/methanogenic organisms as they form. Normally, their concentrations are in the range of 50-250 mg L^{-1} (Sawyer et al., 2003). As long as the pH of the digester remains neutral they can be maintained at levels as high as 10 g L^{-1} (Amani et al., 2010). If there is a disturbance in methanogenesis, VFA's can build up lowering the digester pH. If the pH drops too low methanogenesis can be inhibited. If buffering capacity of the digester is maintained, and the pH of the system is neutral, the specific VFA concentration isn't of concern. Addition of alkaline, such as NaOH, can help to raise the pH and correct acidification due to overproduction of organic acids.

1.4.6 Long chain organic acids

Long chain fatty acids (LCFA's) are an energy dense carbon source for the microbes involved in anaerobic digestion. Theoretically, due to their high carbon density,

they yield the most methane of any substrate. However, at increased concentrations they can have a toxic effect (Khanal, 2008). LCFA's cause problems due to their hydrophobicity. They can dissolve into bacterial cell walls and inhibit cell activity, specifically transport and protection (Gerardi, 2003; Rinzema et al., 1994). Most long chain fatty acids are in the form of insoluble calcium salts and are therefore of no concern (McCarty, 1964). However, large sporadic inputs of oil of grease can cause problems with biogas production (Neves et al., 2009). A concentration of LCFA's greater than 500 g L^{-1} can cause toxicity in an anaerobic digester (Gerardi, 2003).

1.4.7 Heavy metals

Soluble heavy metals are more toxic than their insoluble forms. Although necessary in trace amounts, heavy metals can be toxic when higher concentrations are reached. Since heavy metals do not biodegrade there is the potential for accumulation over time to toxic levels inside the digester. In general, high concentrations of cadmium, cobalt, copper, zinc, nickel and chromium can lead to disturbances in methane production (Deublin and Steinhauser, 2008; Khanal, 2008; Gerardi, 2003). They are listed in order of toxicity below,

$$Ni > Cu > Pb > Cr > Zn$$

Heavy metals adsorb to the surface of bacterial cells and inactivate enzymes by binding to thiol groups or inactivate enzymes by replacing naturally occurring enzymatic metals (Gerardi, 2003; Vallee and Ulner, 1972). Operators of anaerobic digesters can control heavy metal toxicity by diluting the digester, removing toxic materials form the waste, forming insoluble precipitates with sulphides, or deactivating the biological activity by the addition of complexing agents such as EDTA (Deublin and Steinhauser, 2008;

McCarty, 1964). It requires approximately 0.5 mg of sulphide to precipitate 1.0 mg of heavy metal (Khanal, 2008). Therefore, maintaining an adequate sulphide level inside the digester is crucial for preventing heavy metal toxicity.

1.4.8 Light metals

High salt levels can cause bacterial cells to dehydrate due to disturbances in osmotic pressure. Light metals such as sodium, potassium, calcium and magnesium are required nutrients at low levels (Table 1.6). At concentrations above 1000 mg L^{-1} alkali salts can cause inhibition (McCarty, 1964). Acclimation to high salt concentrations can greatly reduce inhibitory effects.

Table 1.6 Concentrations (mg L^{-1}) of alkali cations that will stimulate, inhibit, and strongly inhibit anaerobic digestion (McCarty, 1964; Deublin and Steinhauser, 2008).

Cation	Stimulatory	Moderately Inhibitory	Toxic
Sodium	100-200	3500-5500	8000
Potassium	200-400	2500-5000	12000
Calcium	100-200	2500-7000	8000
Magnesium	75-150	1000-2400	3000

1.4.9 Synthetic organic compounds

Various synthetic organic compounds can inhibit anaerobic digestion. Benzene ring compounds (tannins), chlorinated hydrocarbons, and halogenated aliphatics, and N-substituted aromatics have all been shown to be toxic at varying concentrations, exposure times, temperatures, and biomass concentrations (Chen et al., 2008). Poorly soluble organics tend to accumulate on the surface of sludge solids causing cell membranes to swell and leak (Heipieper et al., 1994). Compounds such as chlorophenols cause toxicity by disrupting proton gradients and interfering with energy transduction (Chen et al.,

2008; Sikkema et al., 1995). Halogenated alphatics, such as chloroform, have been shown to be inhibitory to methanogenesis at levels as low as 0.01mg L^{-1} (Stickley, 1970). N-substituted aromatics inhibit anaerobic digestion by interfering with specific enzymes and chemical pathways (Balderston and Payne, 1976). It should be noted that with most synthetic organic compounds it has been shown that acclimation can reduce inhibition greatly (Chen et al., 2008).

1.5 Advantages of a using anaerobic digestion to treat wastes

The advantages of using anaerobic treatment over aerobic treatment are presented below.

i. Anaerobic treatment of waste produces less sludge. During aerobic digestion 50% of the substrate is converted to biomass and 50% of it to carbon dioxide and water. Anaerobic respiration is much less efficient than aerobic respiration with only 10% of the substrate converted into biomass and 90% converted to wastes and end products. Therefore much less sludge is produced anaerobically than aerobically (Figure 1.1).

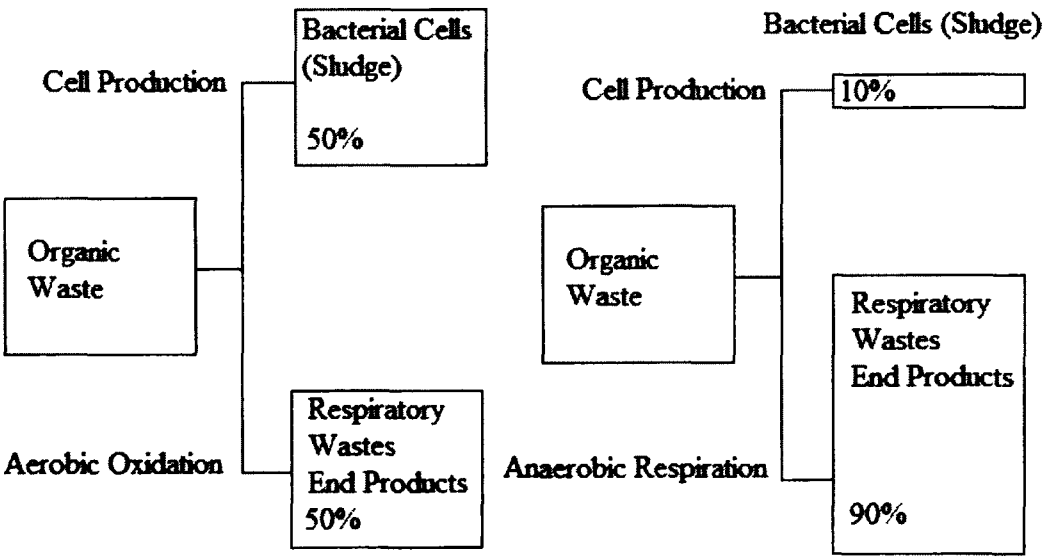

Figure 1.1 Comparison of sludge production between anaerobic treatment and aerobic treatment (Adapted from Gerardi, 2003)

ii. Anaerobic digestion requires fewer nutrients. Due to the production of less biomass anaerobic digestion requires less nitrogen and phosphorous than aerobic digestion. Often N and P must be added for the proper aerobic treatment of wastes lacking these nutrients. This is the case with many industrial effluents such as pulp mill effluent.

iii. Anaerobic digestion is less malodorous. The digestion of substrates must occur in a closed system to exclude oxygen. Therefore, malodorous compounds such as hydrogen sulphide, methylsulphide, and dimethylsulphide are trapped and cleaned from the biogas, or combusted.

iv. Anaerobic digestion reduces the pathogen content of the waste. Pathogen levels in wastes can be reduced as the bacteria, protozoa, and fungi in the digester compete with and overgrow pathogenic organisms (Deublin and Steinhauser, 2008). Thermophilic anaerobic digestion has the added advantage of thermally destroying microbial pathogens present (Smith et al., 2005). Mesophilic anaerobic digestion can also reduce the number of pathogens present in the sludge to a lesser degree (Kearney et al., 1993). Pathogen inactivation is dependant on factors such as temperature, retention period, reactor configuration, microbial competition, pH, and chemical interactions (Smith et al., 2005). Weed seeds found in manure or biomass wastes are also inactivated by anaerobic digestion. Generally, the longer the retention time of the sludge the greater the inactivation of weed seeds (Jeyanayagam et al., 1984).

v. Anaerobic digestion has a positive ("clean") energy balance. When compared to aerobic digestion, anaerobic digestion has a net positive energy balance (Khanal, 2008). The energy requirements for the aeration of aerobic systems can account for up to 75% of the total wastewater treatment plant energy costs (Reardon, 1995). Excess methane

produced from the AD process can be used as a fuel. Most often biogas is used in a combined heat and power (CHP) system to offset the energy requirements of waste treatment. Waste heat can be used for heating the anaerobic digesters and other accessory buildings. Excess electricity produced can be sold to the grid. The most commonly used CHP systems are the four stroke engine, gas-diesel engine, Stirling engine, gas turbine, and fuel cell (Deublin and Steinhauser, 2008). Biogas can also be upgraded and used as a vehicle fuel or sold to the natural gas grid. The biogas produced is considered carbon-neutral because carbon dioxide released during its combustion was captured from the atmosphere during previous biomass growth (Muradov and Veziroglu, 2008). Energy produced from the anaerobic digestion of wastes may even be considered carbon negative since methane (approximately 20 times more potent greenhouse gas than carbon dioxide) that may have otherwise been generated uncontrolled in a landfill is combusted to form carbon dioxide and water.

vi. Anaerobic digestion produces a nitrogen and phosphorous rich fertilizer.

Dewatered, anaerobically digested sludge, often termed biosolids, can contain up to 6% total N and 3% phosphorous by weight as well a many trace nutrients and heavy metals (Deublin and Steinhauser, 2008). Application of biosolids has been shown to act a fertilizer improving soil fertility and plant growth (Singh and Agrawal, 2008; Prescott and Belvins, 2005; Cogger et al., 2001). Application of biosolids to farm land can be seen as closing the nutrient loop (Figure 1.2).

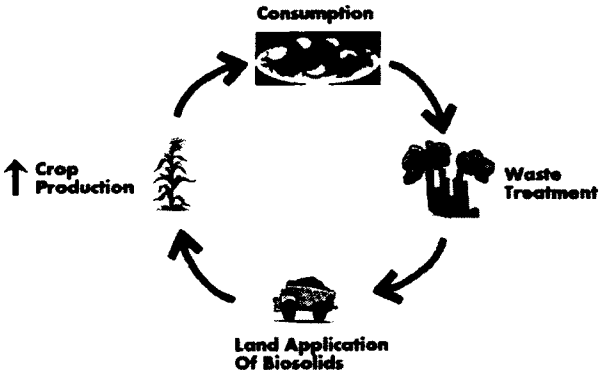

Figure 1.2 Land application of biosolids and the nutrient loop.

Care must be taken when applying biosolids to land to ensure that trace elements, organic pollutants, and excess N and P do not cause detrimental effects. Many countries have strict regulations regarding the land application of biosolids in order to minimize loss of nutrients from the loop and their possible negative effects on waterways, plants, and animals (Iranpour et al., 2004).

1.6 Disadvantages and limitations of anaerobic digestion

i. Anaerobic digestion has significant capital and operational costs. Often, the capital and operational costs of running an anaerobic digestion program solely for energy production make the process uneconomical. AD must be considered as part of an entire waste treatment system with other benefits besides energy production such as; volume reduction, odour reduction, fertilizer production, pollution control, and waste heat/carbon dioxide utilization.

ii. Anaerobic digestion has a slow initial start-up time. Due to the low biomass volume (sludge volume) produced anaerobic digestion requires a long start up time in order to achieve optimum biomass concentrations in the digester. The start-up phase of an anaerobic digester can last 2 to 4 months (Deublin and Steinhauser, 2008).

ii. Anaerobic digestion is vulnerable to disturbances and recovery times can be long. Methanogenic organisms are very sensitive to environmental factors and the recovery of a digester from failure can take a long time. For this reason AD requires considerable operator attention.

1.7 Anaerobic digestion, global warming, and renewable energy

Global demand for energy is on the rise and is expected to increase 49%, from 522 to 780 quadrillion kJ by the year 2035 (IEA, 2010). The majority of the energy consumed in the next 15 years will be supplied by coal, natural gas, and liquid fossil fuels (IEA, 2010). The intergovernmental panel on climate change (IPCC) has reported that fossil fuel use, since the 1850's, has lead to a rapid increase in atmospheric carbon dioxide emissions (IPPC, 2011). Increased carbon dioxide emissions have contributed to a rise in the average global temperature (IPCC, 2011). An increase in average global temperature may negatively affect human populations by raising sea levels, increasing the risk of flooding in some areas, increasing the chance of extreme weather events, by placing stress on water resources in certain places, increasing the rate of plant and animal species extinction, and by decreasing crop production in seasonally dry and tropical regions (IPCC, 2007). The use of renewable energy, such as anaerobic digestion, for electrical, thermal, and transport energy has the potential to help mitigate climate change by reducing net greenhouse gas emissions (IPCC, 2011). Thus, the use of anaerobic digestion as a renewable energy source has the ability to both reduce the amount of pollution from municipal and industrial sectors while simultaneously producing a consistent, renewable, carbon neutral energy source that can help reduce carbon dioxide emissions and the risks associated with rising global temperatures.

1.8 Anaerobic digestion and the municipal sector

It is estimated that municipal wastewater contains approximately 10 times the energy required to treat it (Shizas and Bagley, 2004). Surprisingly, almost all wastewater treatment plants in North America are net energy users. In the United States, wastewater treatment consumes 21 billion kWh of electricity per year (Kalogo and Monteith, 2008). The majority of the energy content of wastewater is contained in the organic solids, or sludge portion. Energy can be recovered from sewage sludge by gasification, incineration, pyrolysis, and/or anaerobic digestion (Kalogo and Monteith, 2008). A combination of processes is preferred in order to extract as much energy from the sludge as possible.

During the last twenty years the government of Canada has been continuously improving the level of wastewater treatment in Canada (Environment Canada, 2010). This has been achieved by building new wastewater treatment plants where wastewater treatment was not used, by upgrading existing wastewater treatment facilities to higher levels of treatment, and through the introduction of new treatment technologies. Since 1983, Canada has increased the percentage of the population with access to secondary water treatment from 40% to 70% while at the same time reducing the amount of people with no treatment from 30% to 2% (Environment Canada, 2010). Increased secondary treatment and increased access to wastewater treatment have consequently increased the production of sewage sludge. Approximately 389,000 dry tones of sewage sludge are produced each year in Canada (CH2Mill, 2000). Approximately 43% of this sludge is applied to land, 47% of it is incinerated, and 4% is sent to landfills (Apedaile, 2001). A small amount is also used for reclamation purposes. Land application and incineration

have garnered considerable negative public opinion due to concern over environmental contamination and health risks (Nazareth et al., 2003). Economically, sewage sludge disposal can account for more than 50% of the total cost of wastewater treatment (Rulkens, 2004). Therefore, the benefits of using anaerobic digestion to treat waste are twofold; waste volume reduction and energy production.

1.9 Food waste and co-digestion

It is estimated that 38% of all food available for retail sale is wasted in Canada (Statistics Canada, 2008a). The Canadian food system (farm production, food processing, and preparation) accounts for about 11% of Canada's total energy demand (CAEEDAC, 2000). Not accounting for food transport, or waste disposal, food waste compromises approximately 4% of Canada's total energy demand. Considering how energy intensive the food system is, it is surprising that little or no energy is recovered from wasted food. Some energy is recovered through incineration along with municipal solid waste; however, the high water content limits the amount of energy that can be recovered from food waste. The majority of food waste is disposed in landfills where it is allowed to decompose uncontrolled, contributing potent greenhouse gases to the atmosphere such as methane.

The high water content and high nutritional value of food waste makes it an ideal substrate for anaerobic digestion (Zhang et al., 2007). However, fruit and vegetable waste has been shown to be too easily biodegradable on its own (Bouallagui et al., 2005). Therefore, anaerobic digestion of food waste must be performed with a co-substrate with a high buffering capacity in order to prevent VFA acidification. The anaerobic digestion of two or more different waste streams is termed co-digestion.

The benefits of co-digestion include: dilution of potential toxic compounds, improved nutrient balance, synergistic effects of microorganisms, increased load of biodegradable matter, and ultimately increased biogas yield (Sosnowski et al., 2003). Often, the C/N ratio of wastes is not ideal for anaerobic digestion. The ratio should be in the range of 16:1 to 25:1 (Deublin and Steinhauser, 2008). Addition of a high C substrate such as vegetable waste or straw can raise the carbon\nitrogen ratio of a carbon deficient substrate. Addition of a highly nitrogenous substrate, such as manure or slaughterhouse waste, can decrease the carbon to nitrogen ratio of a high carbon substrate. Addition of co-digestate provides excess nutrients which maximize microbial activity and subsequent biogas production. Zitomer et al. (2008) have shown that brewing waste yeast extract can increase the biogas production in an operational wastewater treatment plant much more than theoretically expected by added COD only. The authors hypothesize that the addition of trace nutrients such as Co, Fe, Ni may have produced synergistic effects.

As well as improving the yield of biogas, co-digestion can improve the dewaterability and degree of stabilization of the final biosolids (Habiba et al., 2009). Often, the biogas output of existing facilities treating a single waste stream can be greatly improved with little or no capital investment by the implementation of co-digestion (Zupancic et al., 2008). Economically, combined use of wastewater treatment equipment for treating liquid and solid waste can be advantageous (Hamzawi et al., 1998). Co-digestion at facilities treating municipal wastewater sludge are of particular interest because of the low solids content, low C/N ratio, and low nutritional value of municipal sludge. These parameters can be optimized by co-substrate addition. There has been great interest on co-digestion in the last few years. Research papers with the word, "co-

digestion" in the title have quadrupled in the last four years (Mata-Alvarez et al., 2011). Table 1.7 outlines a number of full scale co-digestion applications that have been reported in the literature. Table 1.8 outlines a number of co-digestion studies at the lab scale.

Table 1.7 Full scale co-digestion studies utilizing organic waste that have been reported in the literature since the year 2000. (OFMSW-Organic fraction of municipal solid waste. SS- sewage sludge. OLR- organic loading rate. FVW-fruit and vegetable waste. FW-Food waste. BW- Brewery waste. AR- Agricultural residues. NR-Not reported)

Substrate	Increase in OLR	Increase in Biogas Production	Comments	Reference
OFMSW SS	0.2 kg m^{-3} d^{-1} 25% increase	0.2-0.5 m^3 kg^{-1} VSS fed 80% increase	- Increased VSS degradation by 10% - No increase in VSS of effluent	Zupancic et al., 2008
OFMSW SS	0.2 kg VS m^{-3} d^{-1} 20% increase	0.54 m^3 kg^{-1} VS fed 50% increase	- Methane content of biogas increased	Bolzonella et al., 2006
OFMSW SS	0.32 kg VS m^{-3} d^{-1} 40% increase	0.77 m^3 kg^{-1} VS fed 500% increase	- 8-9 tons of OFSW per 80-90m^3 sludge - Digester was co-digesting for 2 years	Bolzonella et al., 2006
FW SS	3-6 kg VS m^{-3} d^{-1} 23% increase	0.6-0.79 m^3 m^{-3} d^{-1} 43%	- No negative impact of digester performance - HRT decreased from 15.4-7.5	Kubler et al., 2000
FVW SS	NR 20%	0.049 m^3 d^{-1} 27%	- Utilized supermarket FVW - Small digester volume (240m^3)	Edelmann et al., 2000
Manure AR	2.14 kg VS m^{-3} d^{-1}	1.41 m^3 $m^{-3}d^{-1}$	- Co-digested agricultural residues - Electrical output of the plant doubled	Lindorfer et al., 2008
FW SS	NR	Average of 755 m^3 d^{-1}	- 7% of plants electrical requirement - 42% volatile solids destruction (VSD), 60% CH4	Yoneyama and Takeno, 2002
BW /FW SS	NR	70% increase	- extra 16,000 kwh d^{-1}, worth $200,000 - only 1% increase in COD	Zitomer and Adhikari, 2005

Table 1.8 Lab scale co-digestion studies utilizing organic waste that have reported in the literature since the year 2000.

Operation	Substrate	Increase in OLR	Increase in Biogas Production	Comments	Reference
Batch	FVW SS	NR	0.18-0.732 L g^{-1} VS fed	- Majority of 54 FVW had yields > 0.3 L g added - Lemon seeds exhibited highest 0.732L /g VS added	Nallathambi Gunaseelan, 2004
Batch	FVW SS	NR	0.68 L g^{-1} VS fed 1.04 L g^{-1} VS removed	- Co-digestion performed better than individual substrates alone.	Anhuradha et al., 2007
Batch	FW SS	1-4 g VS L^{-1}	0.116-0.257 L CH_4 g^{-1} VS removed	- 40% food waste by VS was optimum - increased gas output was due to additional C	Kim et al., 2003
Batch	FW SS	4 g VS L^{-1}	0.239 L g^{-1} VS removed	- Industrial FW (pig slaughter and FVW screening) - Optimum C:N was 15:1	Siddiqui et al., 2011
Batch	FW SS	197 g VS L^{-1}	0.49 L CH_4 g^{-1} VS	- 20% TS 30% SS - 30-50% VSD	Forster-Carneiro et al., 2008
Batch	FW SS	0.5 g VS L^{-1} d^{-1}	0.29 L CH_4 g^{-1} VS fed	- 60% VSD	Altinbas et al., 2010
Batch	FW SS	25-45 g VS L^{-1}	0.43 L CH_4 g^{-1} VS fed	- BMP tests - 90% FW by VS produced maximum methane	Heo et al., 2003
Batch	FVW/FW	NR	0.69-0.79 L g^{-1} VS fed	- Low food to microorganism ratio	Scaglione et. al., 2008
Batch	FW SS	3.1 g VS L^{-1}	0.43 L g^{-1} VS	- Varying F/M ratio - 50% VSD, 25 days HRT	Liu et al., 2009

Table 1.8 Continued.

Operation	Substrate	Increase in OLR	Increase in Biogas Production	Comments	Reference
Batch & Semi-continuous	OFMSW SS	0.392-3 g VS L^{-1} d^{-1}	0.4-0.6 L g^{-1} VSS fed	- Semi continuous was two stage and more effective - Slower biogas production at high OLR	Sosnowski et al., 2003
Pilot Scale	OFMSW	2.8 g VS L^{-1}	0.3-0.4 L g^{-1} VS	- No statistical differences between housing types, area, kitchen wrapping materials, or sorting	Davidsson et al., 2007
Batch (pilot)	FVW SS	160 g VS L^{-1}	0.09 L g^{-1} VS fed	- Room temperature, Low COD removal (20%) poor results. No mixing, high OLR.	Rizk et al., 2007
Batch (pilot)	OFMSW SS	24.5 g VSS L^{-1}	0.439 L CH_4 g^{-1} VSS d^{-1}	- OFMSW inhibited due to VFA accumulation - Stable production due to buffering capacity of SS	Sosnowski et al., 2008
Batch (pilot)	FVW/KW SS	0.77 to1.13 g L^{-1} d^{-1} 0-23% increase	0.15 to 0.45 m^3 L^{-1} d^{-1}	- 24-33% VSD - % CH_4 decreased from 63 to 58%	Caffaz et al., 2008
Batch & Continuous	FVW SS	3.07 g VS L^{-1}	0.29 L CH_4 kg^{-1} VS 0.63 L g^{-1} VS removed	- 30 day BMP - VSD 67%	Lin et al., 2010
Batch & Continuous	FW SS	1-3 g VS L^{-1} 0.5 -1.0 g VS L^{-1} d^{-1}	0.53-0.75 L g^{-1} VS 0.3 L g^{-1} VS	- Increasing F/M ratio increased gas production. - NaOH required to control pH. 80% VSD	Chen et al., 2010
Batch & Continuous	FW SS	NR 1.5-5.5 g L^{-1} d^{-1}	NR 0.288 L g^{-1} VS fed	- 80% VSD - 70-80% VSD	Mohan and Bindhu, 2008
Continuous	FVW SS	2.5-3.5 g VS d^{-1}	0.6-0.8 L g^{-1} VS removed	- Low mixing was found to be most favorable	Gomez et al., 2006
Semi-continuous	FVW SW & M	1.1-1.3 g VS L^{-1} d^{-1}	0.002- 0.35 L CH_4 g^{-1} VS fed	- FVW, manure, and SW in various mixtures. Performed better than substrates alone except FVW SW (1:1)	Alvarez and Liden, 2008

Table 1.8 Continued.

Operation	Substrate	Increase in OLR	Increase in Biogas Production	Comments	Reference
Semi-continuous (pilot)	FW SS	19.4 g VS d^{-1}	0.5-0.53 L g-1 VS	- Source sorted supermarket waste	Corti and Lombardi, 2007
Semi-continuous	FVW SS	1.5- 5.9 g VS L^{-1} d-1	0.6 L g-1 VS	- Process overload at 4.4, 5.3, and 5.9 g VS L^{-1} d^{-1}	Murto et al., 2004
Semi-continuous	FVW SS	NR	0.0072 L g-1 VS fed	- 68% VSD over 30 days, yield was very low	Saev et al., 2009
Semi-continuous	OFMSW SS	7.4-8.4 g VS L-1 d-1	0.41-0.51 L g-1 VS fed	- Improvement of VSD over each individual substrate - 6- 22% SS, 22% SS was ideal	Garcia et al., 2010
Sequencing Batch	FVW SS	2.51 g VS L-1 d-1	0.58 L g-1 VS removed 0.49 L g-1 VS fed	- 43% increase in biogas due to better C/N ratio (22-25) - WAS improved buffering capacity of FVW	Bouallagui et al, 2009
Sequencing Batch	FVW	0.3 -3.5 g VS L-1 d-1	0.29-0.57 L g-1 VS removed	- Improved filterability of final sludge	Habiba et al., 2009

There have been very few full scale co-digestion examples reported in the literature, especially at wastewater treatment plants (Mata-Alverez et al., 2011). Chapter two of this thesis represents a six week study co-digesting supermarket waste in the anaerobic digester of a fully functioning wastewater treatment plant.

Chapter three of this thesis was determined after the completion of the full-scale study to determine the optimum digester (first or second stage) in which to add co-digestate.

1.10 Anaerobic digestion in the pulp and paper industry

In 2007, over 5 billion cubic meters of water were used industrially in Canada (Statistics Canada, 2007). The pulp and paper industry takes in the most water of any Canadian industry accounting for almost 38% of the total (Statistics Canada, 2007). This water is used to dissolve wood fibers and produce pulp. It is estimated that the pulp and paper industry accounts for almost 50% of all waste discharged into Canadian waters (Sinclair, 1990). Sludge production from the aerobic treatment of pulp and paper effluents is estimated at almost 1.5 million dry tons annually (Marche et al., 2003). Anaerobic digestion is not widely used in the pulp and paper industry due to the long retention times required to treat secondary sludge and the low degradability of pulp primary sludge. However, recent advances in the pre-treatment of secondary wastewater sludges prior to anaerobic digestion have renewed interest in the use anaerobic digestion to treat pulp mill sludge.

1.11 Pre-treatment of pulp sludge

Microbial cell walls are composed of peptidoglycan; glycan strands cross-linked with peptide chains. Peptidoglycan provides strength to the cell wall and resistance to

degradation. Due to the resistant nature of bacterial cells, hydrolysis is considered the rate limiting step when dealing with biological sludges (Eastman and Ferguson, 1981; Shimizu et al., 2004). The pre-treatment of sludge can increase the hydrolysis rate of secondary sludge by using mechanical, chemical, biological, or thermal forces to break apart sludge flocs and rupture cell walls. Pre-treatment solubilizes cell components making them more easily consumed by anaerobic organisms. Disintegrating floc structure and destroying cell walls also provides easier access to the hydrolytic enzymes that are released during anaerobic digestion promoting breakdown of the sludge. The advantages of pre-treating sludge are listed below (Deublin and Steinhauser, 2008).

i. Increase in the yield of biogas: Organic matter found inside large floc structures or protected behind cell walls is not easily digestible. Pre-treatment increases the proportion of easily accessible organic matter to anaerobic organisms shortening the hydrolysis phase. Therefore biogas is produced more quickly reducing the HRT.

ii. Increase in the degree of sludge decomposition: Increased access to internal cell components, and increased biogas production, ultimately lead to a greater VS destruction rate. An increased VS destruction rate leads to less sludge.

iii. Sludge viscosity is lowered: Increasing the degradation rate of the sludge lowers the viscosity due to the lower solids content of the sludge. Pumping, heat transfer, and mixing require less energy.

iv. Reduction in foaming and floating sludge: Pre-treatment can destroy filamentous organisms that cause foaming. Also, large flocs that trap gas bubbles are destroyed reducing the amount of floating sludge.

Some of the disadvantages of employing sludge pre-treatment are explained below (Deublin and Steinhauser, 2008):

i. Dewaterability can decrease: As sludge flocs are made smaller they become harder to dewater due to their larger surface area.

ii. Increase in nutrient back load to wastewater treatment plant: Rupturing cell walls releases N, P, and C into the wastewater. Nitrogen and carbon backload can increase by up to 30% and 40% due to pre-treatment, respectively (Deublin and Steinhauser, 2008). In a municipal wastewater treatment plant the minimization of N and P are crucial to the wastewater treatment plant maintaining appropriate effluent regulations. Thus, pre-treatment can be detrimental. In an industrial setting, such as pulp and paper wastewater treatment, wastewater requires nutrient addition to facilitate microorganism growth. Increased back load of N and P can be helpful by reducing the amount of external inorganic fertilizer required for aerobic treatment.

ii. Power consumption of the treatment plant is increased: Pre-treatment of sludge requires energy. The higher the level of disintegration achieved the greater the amount of energy required. Careful consideration must be taken to ensure that the benefits of sludge pre-treatment outweigh the energy costs associated with pre-treatment.

The effectiveness of sludge pretreatment is often measured by the proportion of soluble COD compared total COD. Increasing the pre-treatment energy will increase the ratio of sCOD/tCOD to a point. Sometimes physical characteristics are used to evaluate sludge disintegration such as particle size distribution and microscopic evaluation (Figure 1.3).

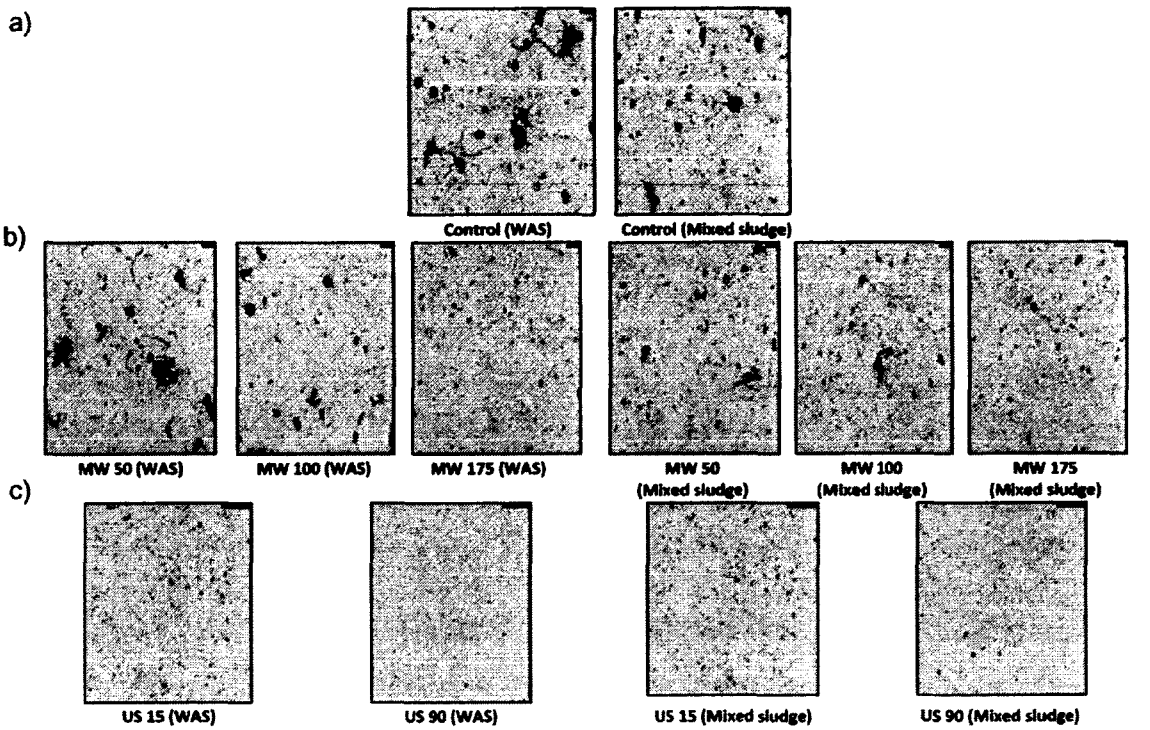

Figure 1.3 Effects of disintegration on pulp mill waste activated sludge and mixed primary and secondary waste activated sludge particle size distribution after a) no treatment b) various intensities of microwave pretreatment and c) various intensities of ultrasound pretreatment (Saha et al., 2011).

1.12 Alkali pre-treatment

Alkali pre-treatment leads to the saponification of cell walls and internal cell components making them soluble and therefore more easily hydrolysed (Deublin and Steinhauser, 2008). Alkaline pre-treatment has been shown to solubilize sludge on its own, but it is more often combined with other pre-treatment methods to improve their effectiveness (Saha et al., 2011; Wood et al., 2009; Chiu et al., 1997). Alkaline pre-treatment has been shown to be especially good at degrading complex wastes such as lignocelluloses (Hendriks and Zeeman, 2009). Lignin is often found in high quantities in pulp mill sludge (20-58%) and cannot be digested easily without pre-treatment (Kyllonen et al., 1988; Deublin and Steinhauser, 2008; Khanal, 2008). Thus, the use of alkaline pre-

treatment on pulp sludge is advantageous for solubilizing both microbial cell walls and recalcitrant lignocellulosic components of the pulp sludge.

1.13 Ultrasound pre-treatment

Ultrasound pre-treatment involves subjugating the sludge to high frequency sound waves (usually at 20 or 40 kHz). When an ultrasound wave propagates through the sludge it compresses and expands, pushing and pulling the molecules together and apart. When the molecules are pulled apart cavitation bubbles form due to large negative pressure. The cavitation bubbles grow and expand until they collapse and produce very high localized temperatures and pressures (Pilli et al., 2011). Therefore, ultrasonication produces mechanical shear forces through cavitation bubbles which rupture cell walls releasing cellular matter into solution (Elliot and Mahmood, 2007).

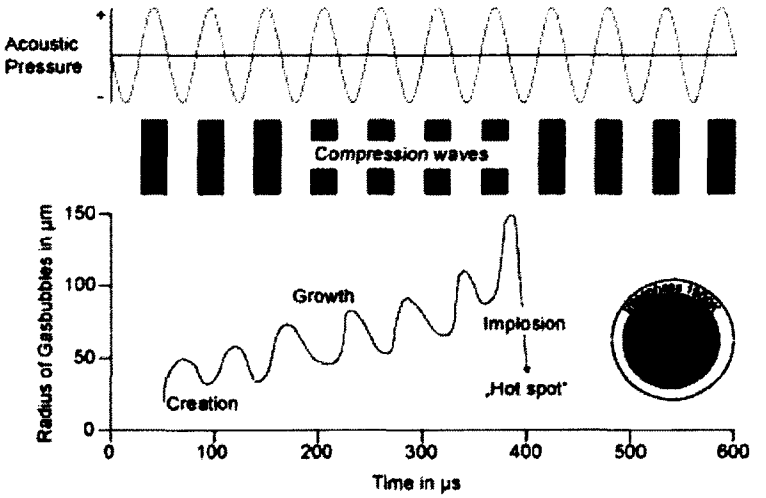

Figure 1.4 Development and collapse of the cavitation bubble (Sonotronic Technologies).

In addition to mechanical shear forces, sonochemical reactions occur in the sludge that produce highly reactive free radicals such as $OH\cdot$, $HO_2\cdot$, and $H\cdot$ (Khanal, 2008). The oxidizing effect of the hydroxyl radical also contributes to sludge disintegration (Pilli et

al, 2011). However, the effect of the hydroxyl radical oxidation has been shown to be quite small compared to the effect of cavitation (Pilli et al., 2011; Wang et al., 2005).

Thickening of sludge prior to ultrasonication can have a considerable effect on the level of sludge disintegration. Increasing the solids content up to 3-4% improves sCOD release; a TS content of over 4% was found to be detrimental to pre-treatment effectiveness (Mao et al., 2004; Show et al., 2007; Nies et al., 2000). Sludge viscosity increases with increasing TS content thus improving energy adsorption and increasing pre-treatment effectiveness. However, if the solids concentration is too high cavitation formation and propagation can be hampered (Show et al., 2007).

One negative consequence of ultrasound treatment is its effect on dewaterability. At low energies (without considerable cell lysis) dewaterability is improved, but at higher energies dewaterability decreases with increasing energy input (Pilli et al., 2011). As cells are lysed smaller particles are released and formed which produce a larger surface area for holding water and are thus more difficult to dewater (Chu et al., 2001). Table 1.9 outlines various studies using pre-treatment to increase the biogas production of pulp and paper secondary sludge.

Table 1.9 Studies anaerobically digesting pre-treated pulp mill sludge since the year 2000 (PPS- Primary pulp sludge. SPS- Secondary pulp sludge. SM- Sulphite mill. KM- Kraft mill. NS- Not significant. N/A- Not applicable.).

Operation	Pre-treatment	Substrate	Biogas Production	Biogas Improvement	Comments	Reference
Batch & Continuous	Enzymatic Ultrasound	SPS	0.1-0.2 L CH_4 g^{-1} VS	50% @ 8d 44% @ 4d, NS @ 100d	- ultrasound & enzymatic pre-treatment didn't improve yield - ultrasound improved initial rate of gas production	Karlsson et al., 2011
Batch	None	SPS	0.2 L CH^4 g^{-1} VS fed	N/A	- co-digested with monosodium glutamate waste liquor	Lin et al., 2010
N/A	Alkaline	SPS	N/A	N/A	- sCOD/COD improved from 7.4% to 32% - pre-treatment reduced VSS (21% at 60 meq / L)	Navia et al., 2002
Batch	Microwave Ultasound Microsludge	PPS & SPS	0.12 L g^{-1} COD 0.11 L g^{-1} COD 0.1 L g^{-1} COD	63% 51% 34%	- microwave and ultrasound were not economical - microsludge treated waste lost 23% VS during pre-treatment	Saha et al., 2011
Batch	Thermal Thermochemical Sonication	SPS	SM 0.24 KM 0.19 L g^{-1} COD SM 0.3 KM 0.2 L g^{-1} COD SM 0.18 KM 0.06 L g^{-1} COD	KM:50% SM:280% KM:300% SM:18% KM: NS SM: NS	- sludge from KM and SM - fraction of methane in biogas unchanged - SM produced more biogas than KM	Wood et al., 2009
Batch	Biological	SPS	0.23 L CH_4 g^{-1} VS fed	132%	- co-digested with monosodium glutamate liquor - pre-treated with mushroom compost extract	Lin et al., 2010
Batch	Alkaline	PPS & SPS	0.32 L CH_4 g^{-1} VS removed	184%	- 8g NaOH/100g TS was optimal - sCOD increased 83%	Lin et al., 2009
Batch	None	PPS	0.13-0.42 L CH_4 g^{-1} VS	N/A	- sludges originated from 3 different plants	Parkarinen et al., 2010

Pre-treatment of sludges produced in the municipal sector has been well documented in the literature. Municipal sludge pre-treatment technologies have been demonstrated in many full scale applications (Hogan et al., 2004; Kepp et al., 2000; Stephenson et al., 2005; Froud et al., 2005; Seivers et al., 2004). These full-scale pre-treatment units are available commercially from a range of suppliers. Very little research has been performed on the pre-treatment of pulp sludge (Elliot and Mahmood, 2007). Even fewer reports have been published on the combination of multiple pre-treatment methods for pulp sludge (Table 1.9). The objective of chapter four of this thesis was to determine the effectiveness of combining alkaline and ultrasonic pre-treatment to solubilize thickened and non-thickened secondary sludge obtained from Quesnel River Pulp, B.C., for improved subsequent anaerobic digestion. COD solubilization, biogas production characteristics, and sludge degradation were used to evaluate pre-treatment effectiveness.

Preface

Chapter 2 of this thesis is an extended version of the published article:

Park, N.D., Thring, R.W., Garton, R.P., Rutherford, M.P., Helle, S.S. 2011. Increased biogas production in a wastewater treatment plant by anaerobic co-digestion of fruit and vegetable waste and sewer sludge- A full scale study. *Water Science and Technology* 64(9):1851-56.

CHAPTER 2: Increased biogas production in a wastewater treatment plant by anaerobic co-digestion of fruit and vegetable waste and sewer sludge – A full-scale study

2.1 Abstract

Anaerobic digestion is a well-established technology for the reduction of organic matter and stabilization of wastewater. Biogas, a mixture of methane and carbon dioxide, is produced as a useful by-product of the process. Current solid waste management at the city of Prince George is focused on disposal and not on energy recovery. Co-digestion of fresh fruit and vegetable waste (FVW) with sewage sludge can improve biogas yield by increasing the load of biodegradable material. A six-week full-scale project co-digesting almost 15,000 kg's of supermarket waste was completed. Average daily biogas production was found to be significantly higher than in previous years. Digester operation remained stable over the course of the study as indicated by the consistently low total volatile acidity-to-alkalinity ratio. Undigested organic material was visible in centrifuged sludge suggesting that the FVW should have been added to the first stage digester to prevent "short-circuiting", and to increase the hydraulic retention time of the FVW.

2.2 Introduction

An estimated 38% of solid food available for retail sale was wasted by Canadians in 2007 (Statistics Canada, 2008a). The majority of this organic waste was disposed of in landfills. Issues with landfill space, groundwater contamination, resource sustainability, and greenhouse gas emissions have sparked interest in diversion of waste from landfills. Composting is the most common form of organic waste diversion from landfills in Canada. Approximately 1.7 million tonnes of organic waste were composted in centralized facilities in Canada in 2002 (Statistics Canada, 2008b). Composting produces

a valuable resource as a soil amendment, but is an energy intensive process. Also, recent concerns over energy sustainability, energy security, and anthropogenic climate change have sparked great interest in producing energy from waste. Incineration is the most common form of energy generation from waste. However, the high water content in food waste limits its energy production potential.

Anaerobic digestion (AD) is a process in which bacteria consume organic matter, in the absence of oxygen, to produce methane gas and carbon dioxide. Biogas, as the gas mixture is termed, can be used as fuel like conventional natural gas. The remaining stabilized solids, or biosolids, are beneficial as a nitrogen and phosphorous rich soil amendment. The AD process has been in use for decades to stabilize and reduce the organic solids found in wastewaters. The biogas produced can be used to supplement the energy demands of the wastewater treatment facility. Most municipal AD systems are constructed with excess capacity to account for future population growth and have low organic loading rates due to the low solids content of incoming raw sludge. Total solids content of the digester sludge at the Lansdowne wastewater treatment plant (LWWTP) is approximately 1.5% and could be increased to the 3 - 4% range without significant plant modifications (Garton, 2010). Biogas yield could be improved, with minimal capital investment, by adding biodegradable matter to increase the digester loading. This process is also known as co-digestion.

Anaerobic digestion of organic wastes is a viable waste disposal method to reduce greenhouse gas emissions (Haight, 2005). Due to the sealed and controlled nature of AD, volatile gases are trapped and combusted to form carbon dioxide. Aerobic treatment of wastes, on the other hand, produces large and uncontrolled emissions of volatile

compounds, such as ketones, aldehydes, ammonia and methane (Mata-Alverez et al., 2000). Methane is of significant importance due to the large amount formed during the decomposition of organic wastes and its potent greenhouse gas warming potential (almost 20 times that of carbon dioxide). Anaerobic digestion is therefore advantageous from an emissions standpoint by producing methane in a controlled manner. This methane can then be burnt to produce carbon neutral CO_2 and offset emissions from energy production that may have otherwise come from fossil fuels (Ward et al., 2008).

The benefits of co-digestion include: the dilution of toxic compounds, improved balance of nutrients, synergistic effects of organisms, increased load of biodegradable matter, and ultimately an increase in biogas yield (Sosnowski et al., 2003). Much research has been conducted in the laboratory on the co-digestion of various organic wastes (Ward et al., 2008; Alatriste-Mondragon et al., 2006). Lab scale experiments by Zhang et al. (2007) have shown that food waste is a highly desirable substrate for anaerobic digestion due to its high biodegradability and methane yield. Full scale anaerobic co-digestion projects are less widely reported (Mata-Alvarez et al., 2011).

Zupancic et al. (2008) increased the organic loading rate (OLR) of digester influent by 25% using the organic fraction of municipal solid waste (OFMSW) in a fully operational wastewater treatment plant. Biogas quantity increased by 80%, electrical energy production increased by 130%, and heat production increased by 55%. The increased volatile solids load also improved the volatile solids destruction by 10% and there was no significant increase in digester effluent volatile solids content. Bolzonella et al. (2006) have also increased the OLR of a fully operational WWTP by as much as 20% with the addition OFMSW and subsequently increased gas production by 50%.

Edelmann et al. (2000) found an increase in biogas production of 27% when the organic loading was increased by co-digesting supermarket waste in a relatively small sewage treatment plant.

The full scale study presented here was undertaken to assess the feasibility of using local fruit and vegetable waste to improve biogas production in the anaerobic digesters of the LWWTP in Prince George, British Columbia, Canada. FVW was added to the second stage digester in order to increase the loading of easily biodegradable matter and potentially promote digestion of recalcitrant sludge. The waste was collected from six supermarkets in town; hand sorted, characterized, shredded, and pumped into the second stage digester. Overall digester performance was evaluated during the course of the study.

2.3 Materials and Methods

2.3.1 The Lansdowne wastewater treatment plant (LWWTP) process

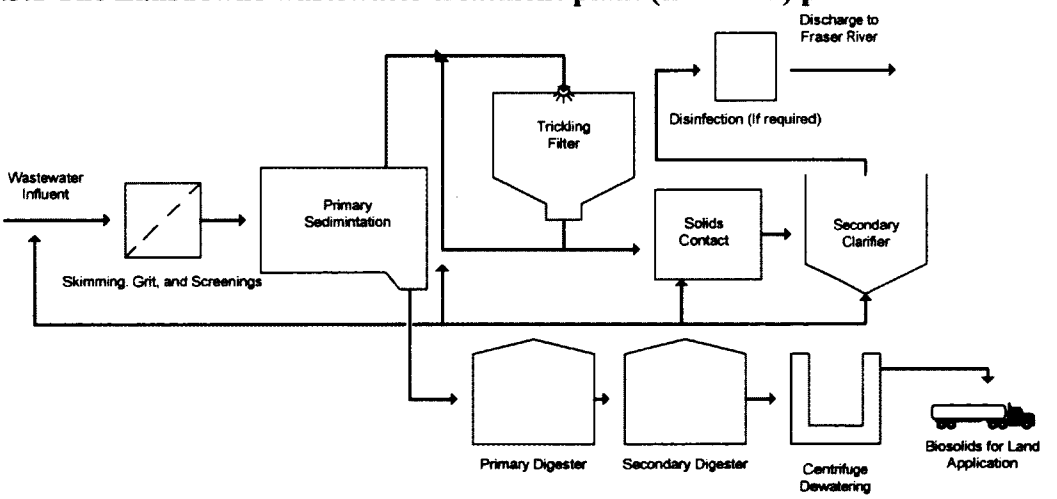

Figure 2.0 The LWWTP plant process.

The LWWTP (Figure 2.0) is a secondary wastewater treatment plant that treats wastewater coming from the municipality of Prince George, British Columbia, Canada.

The plant is sized for 115,000 population equivalents (PE). Digesters are fed approximately 120 $m^3 d^{-1}$ of crude sludge (approximately 3.5-4% TS) from two primary clarifiers. The anaerobic digestion system is composed of two digesters, operated in series, each with a maximum volume of 2986 m^3. The digesters are operated at mesophilic (36 ± 2°C) temperatures. The combined hydraulic retention time of both digesters is approximately 35-40 days. After the sludge has been stabilized it is dewatered by centrifugation to about 25% dry matter. Methane gas is used in a boiler to produce heat, or cleaned of hydrogen sulphide and siloxanes and combusted by as set of microturbines to produce electricity (Figure 2.1). The microturbines are used mainly in the summertime when the heating requirements of the LWWTP are low.

All in-process measurements were performed by the City of Prince George laboratory staff. Combined digester biogas production was measured continuously and totaled daily. Digester gas carbon dioxide concentration is measured 2-3 times per week using a Fyrite™ gas meter. Methane gas concentration is assumed to make up the remaining balance. Total volatile acidity and alkalinity of the digester sludge were determined twice per week by the method outlined by Dilallo and Alberton (1961). Digester sludge pH was measured by standard methods (APHA, 1998).

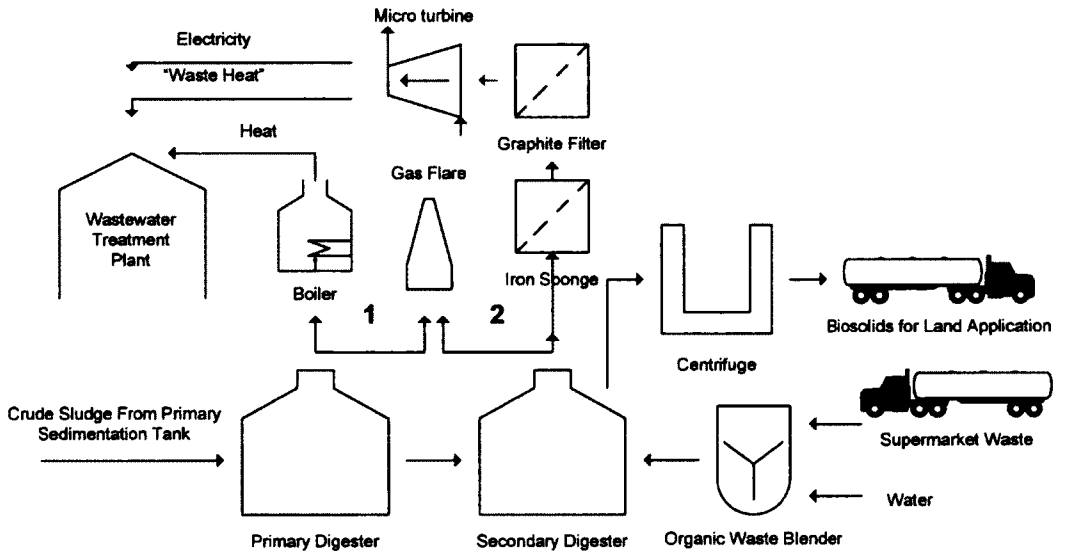

Figure 2.1 Set-up for digester and biogas end use. Biogas is either utilized in boiler (1) or micro-turbines (2), both with excess biogas flared.

2.3.2 Fruit and vegetable waste (FVW) collection and addition

FVW was collected from Save-On Foods (four locations), Shoppers Wholesale, and Old Town Country Market in Prince George; B.C. Waste was collected every weekday morning (excluding statutory holidays). FVW was then spread out on a clean concrete pad and visible impurities were removed by hand. The "clean" FVW was then shoveled into a Vaughn™ "Veggie Chopper" pump, mixed with water, and shredded for 2-4 minutes. The shredded waste was then pumped into the sludge heating recirculation line of the second stage digester.

2.3.3 FVW laboratory analysis

Five to ten kilograms of FVW were selected by random shovelfuls and combined. Approximately 1 kg of roughly chopped FVW was blended to a thick consistency (2-3 minutes) using a Krups™ household blender. Blended waste was then stored at 4 °C and analyzed within 48 hrs. Samples of waste were frozen for COD analysis at the end of the study. The mass of FVW waste inserted was recorded daily. TS, VS, COD, pH, total

volatile acidity, and alkalinity were analyzed in duplicate 3 times per week (randomly). TS, VS, and pH were determined by standard methods (APHA, 1998). Sewage sludge (SS) and FVW were diluted 5:1 and 25:1, respectively, with deionised water for COD measurements. COD was determined by the HACH™ colorimetric method (Hach, 2010). Total volatile acidity and alkalinity were determined by the method outlined Dilallo and Alberton (1961).

2.3.4 Statistical data treatment

Historical mean daily biogas production over the same six weeks was compared to that of the study period using analysis of variance (ANOVA). When p was significant (< 0.05), statistical differences among treatment means were determined using Tukey-HSD test. JMP 8 statistical software (SAS, NC, USA 2010) was used to perform statistical calculations. Microsoft Excel was used to produce the graphs.

2.4 Results and discussion

2.4.1 Fruit and vegetable waste addition

The total mass of FVW inserted weekly is shown in Table 2.0. Impurities were mainly plastic food wrapping, and other garbage. It was removed by hand and the wet mass was recorded daily.

Table 2.0 Characteristics of FVW added to the second stage digester.

Week	FVW (kg)	TS (%)	TS (kg)	VS (%TS)	VS Added (kg)	Impurities (kg)	Impurities (%)
July 12-16	1990	12.5	249	90.0	224	5.1	0.26
July 19-23	2166	12.2	264	89.0	234	1.6	0.07
July 26-30	2801	9.6	270	79.9	215	2.5	0.09
Aug 3-6	2391	11.6	277	86.7	240	6.3	0.26
Aug 9-13	2215	13.0	288	89.7	259	3.6	0.16
Aug 16-20	3036	9.7	296	81.7	242	6.1	0.20
Total	14599	NA	1644	NA	1416	25.2	NA
Mean	2433	11.4	274	86.2	236	4.2	0.17
SD	404	1.4	17	4.3	1	2	0.08

Supermarket waste proved to be a reliable and consistent waste stream. One cubic meter of fresh waste weighed approximately 460 kg. The TS and VS of the collected waste remained stable over the course of the experiment (Table 2.0). Source sorted supermarket FVW was found to be extremely low in impurities when compared to similar waste streams. Kubler et al. (2000) found food waste originating from canteens to be considerably higher in impurities, 5% by mass respectively.

2.4.2 FVW and SSS characteristics

A comparison of the FVW and second stage digester sludge (SSS) characteristics are shown in Table 2.1.

Table 2.1 Characteristics of FVW and SSS.

Parameter	FVW	SSS[a]
TS (%)	11.5 ± 2.5	1.42 ± 0.21
VS (%TS)	86.2 ± 7.5	65.8 ± 1.4
pH	4.6 ± 0.4	7.12 ± 0.07
Total Volatile Acidity (mg L^{-1})	2477 ± 445	171 ± 4
Total Alkalinity (mg $CaCO_3$ L^{-1})	979 ± 359	2713 ± 52
COD (g O_2 L^{-1})	139 ± 39	12.8 ± 0.7*

a) Average values from July 1- Aug 31, 2009 (*average COD determined from 1 sampling of SS)

The high moisture content (MC), approximately 89.6%, of the FVW suggests sufficient water for AD. The high VS content (86%TS) imply a high level of biodegradability. TS and VS (Table 2.1) of the supermarket waste were found to be similar to waste collected from similar sources. Bouallagui et al. (2005) reviewed the characteristics of a number of mixed fruit and vegetable wastes and found it them to have a TS content between 8-10%, a VS content of about 90%, and total COD around 104 g O_2 L^{-1}. More variable waste streams such as OFMSW were found to be much higher in TS content, approximately 23-35%, and lower in VS, 57-70% when compared to FVW (Kubler et al., 2000).The VS content of the FVW was approximately 20% higher than the SSS. This suggests that the FVW is more degradable than the sewage sludge. The total volatile acidity concentration of the FVW was quite high suggesting that the FVW may not have had the buffering capacity to maintain optimal pH if anaerobically digested alone (Ward et al., 2008). Co-digestion with a high buffering substrate such as sewage sludge was therefore necessary.

2.4.3 Digester performance and response

Average daily biogas production for the study period under investigation (July 12-Aug 20, 2010) was compared to the historical biogas production during the same period

(Figure 2.2) and was found to be significantly greater than 2008, 2007, and 2006, but not 2009. More stable gas production was observed during addition of FVW than in previous years as seen by the lower standard deviation. Addition of co-digestate may have helped to stabilize gas production by providing easily digestible matter and possibly other trace nutrients that may have been lacking in the second stage sewage sludge.

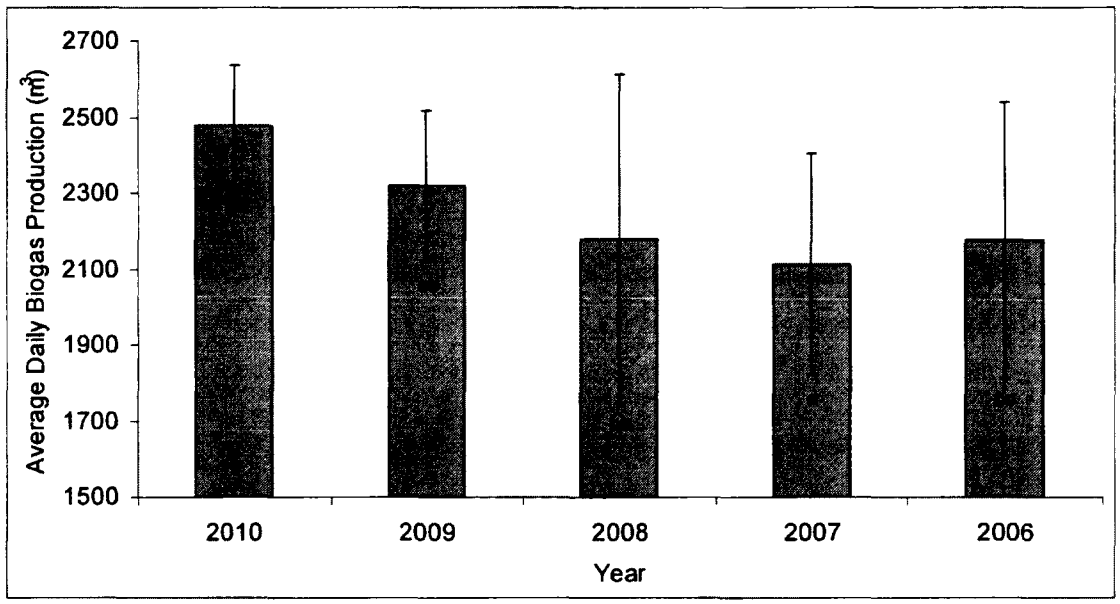

Figure 2.2 Average daily biogas production during the addition of FVW (July 12- Aug 20, 2010) compared to previous years without addition (Means with the same letter are not significant at $p < 0.05$).

The average weekly biogas concentrations for 2010 were 8-17% higher than the historical weekly average (Figure 2.2). Not enough FVW could have been added to account for all of the increased biogas production. Other factors may have contributed to the increase in biogas. Sownoski et al. (2006) suggest that besides added biodegradable matter co-digestion can improve biogas yield by dilution of toxic compounds and improving the balance of nutrients inside the digester. The most important parameter that contributes to biogas production is the volume of crude sludge that flows into the digesters. Sludge volume flow to the digesters, over the last year, was directly

proportional to an increase in biogas production (data not shown). The average daily crude flow of sludge into the digesters was not significantly higher in 2010, during the study period, than any of the previous years (Figure 2.3). Therefore, the increase in biogas production in 2010 cannot simply be accounted for by an increase in flow of crude sludge alone.

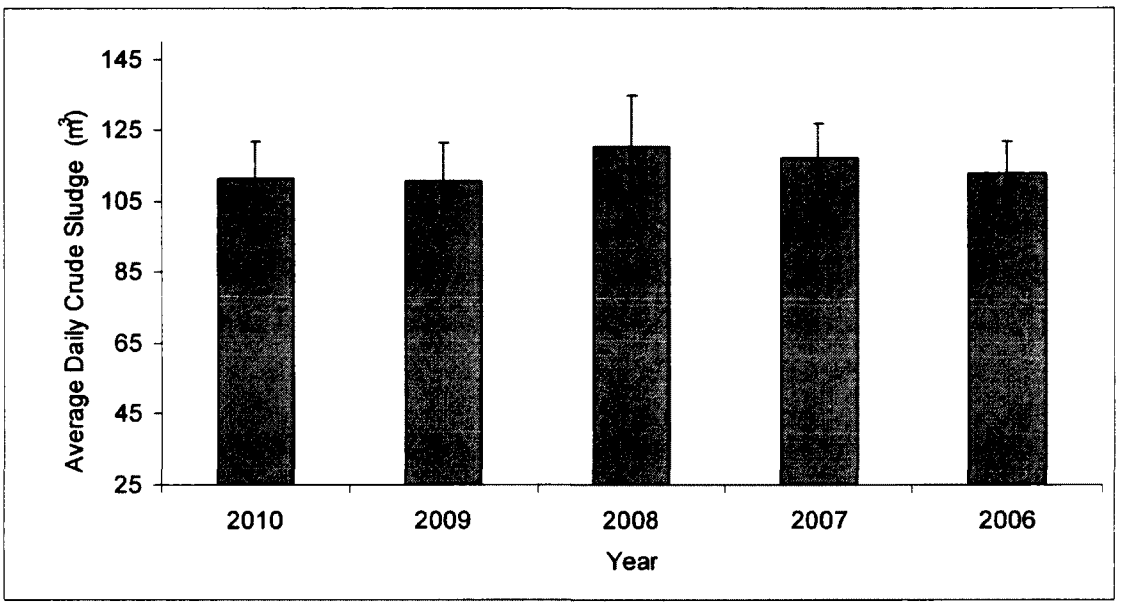

Figure 2.3 Average daily flow of crude sewage sludge to the first stage digester during the addition of FVW (July 12- Aug 20, 2010) compared to previous years without addition (Means with the same letter are not significant at $p < 0.05$).

Digester pH remained relatively stable over the course of the study (Figure 2.4). The second stage digester's pH declined slightly when compared to the first stage digester. This was most likely due to the addition of fresh organic matter. Highly biodegradable matter such as FVW can cause acidification of the digester due to rapid hydrolysis, acidogenesis, and subsequent increase in the volatile acids concentration of the sludge (Ward et al., 2008). However, only a small amount FVW was added to the

digester and the strong buffering capacity of the SSS would have prevented any large shifts in pH.

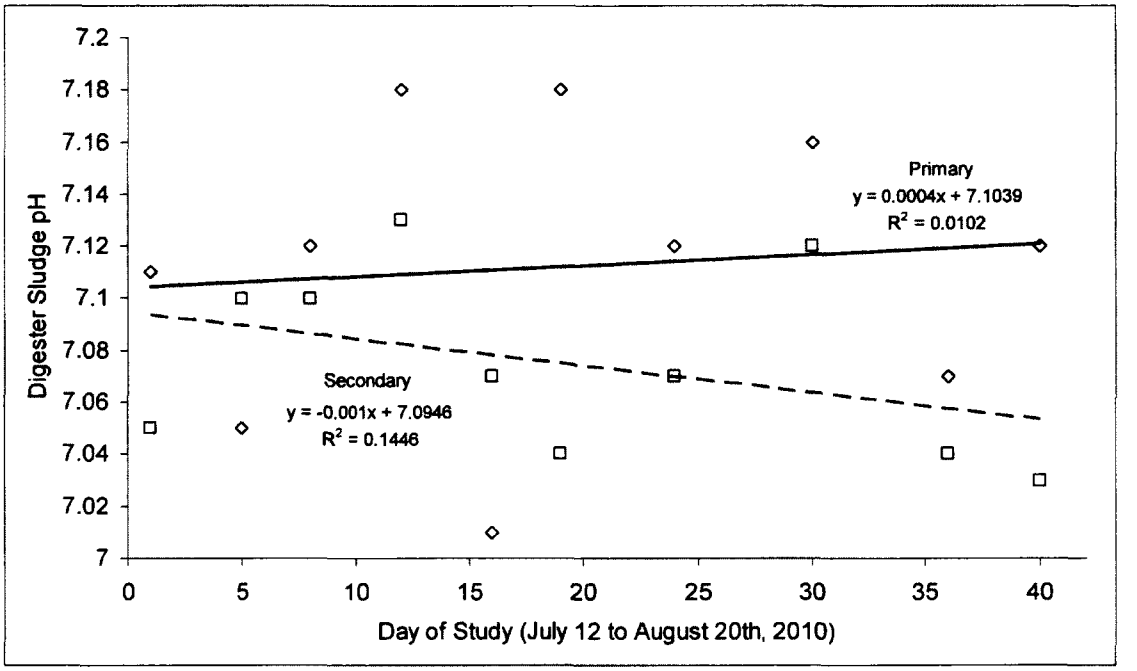

Figure 2.4 First and second stage digester sludge pH over the course the study. □ Second stage digester pH. ◊ First stage digester pH.

As seen in Figure 2.5, there is an increase in the second stage digester carbon dioxide concentration after addition of FVW to the digester. This increase may have been due to the increased hydrolysis and acidogenesis occurring because of the addition of fresh waste. Addition of FVW occurred between Monday and Friday; thus the drop in carbon dioxide concentrations on the weekends. It should be noted that the carbon dioxide concentration of the second stage digester biogas is quite variable.

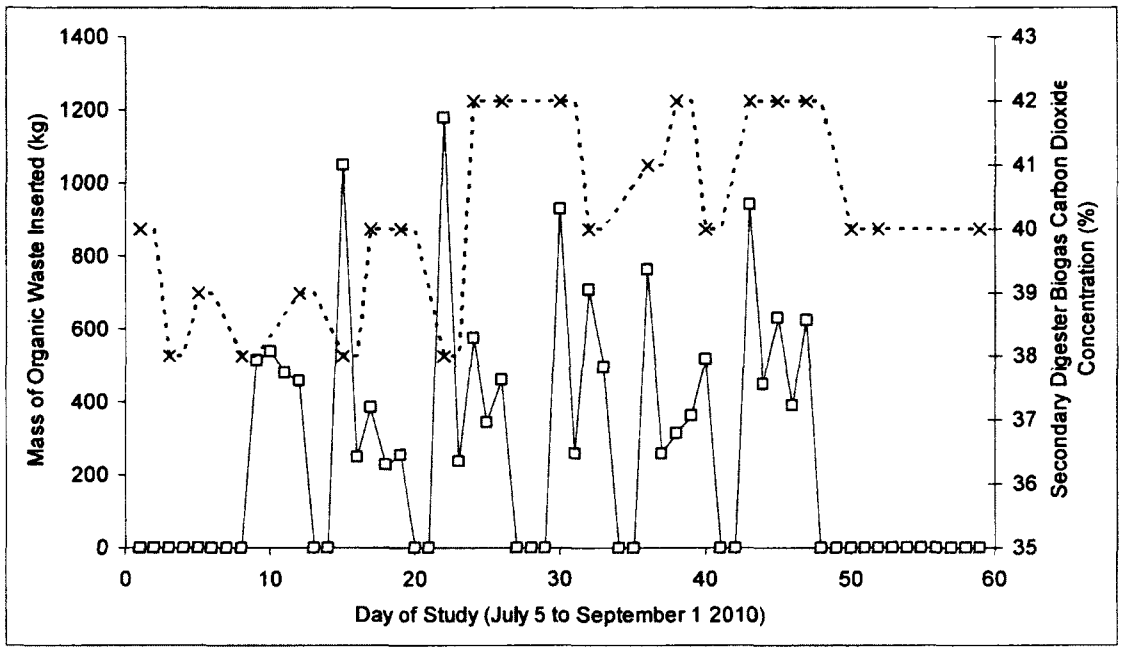

Figure 2.5 Second stage digester biogas carbon dioxide concentration over the course the study (July 12 – August 20, 2010). The dashed line represents carbon dioxide concentration. The solid line indicates the mass of FVW inserted.

The total volatile acidity of the second stage digester generally followed the trend of the primary, but was overall lower (Figure 2.6). Alkalinity remained stable. The lower VS content of the second stage digester is due to decreased sludge activity and formation of volatile acids when compared to the primary digester. Digester health is often determined by the ratio of total volatile acidity to total alkalinity. Ratios of 0.3-0.4 are indicative of digester upset (Water Environment Federation, 2008). The volatile acids to alkalinity ratio of both digesters remained stable (0.06-0.08) throughout the study due to the high alkalinity and buffering capacity of the sewage sludge (Table 2.1). This suggests that more co-digestate could have been added without subsequent digester acidification.

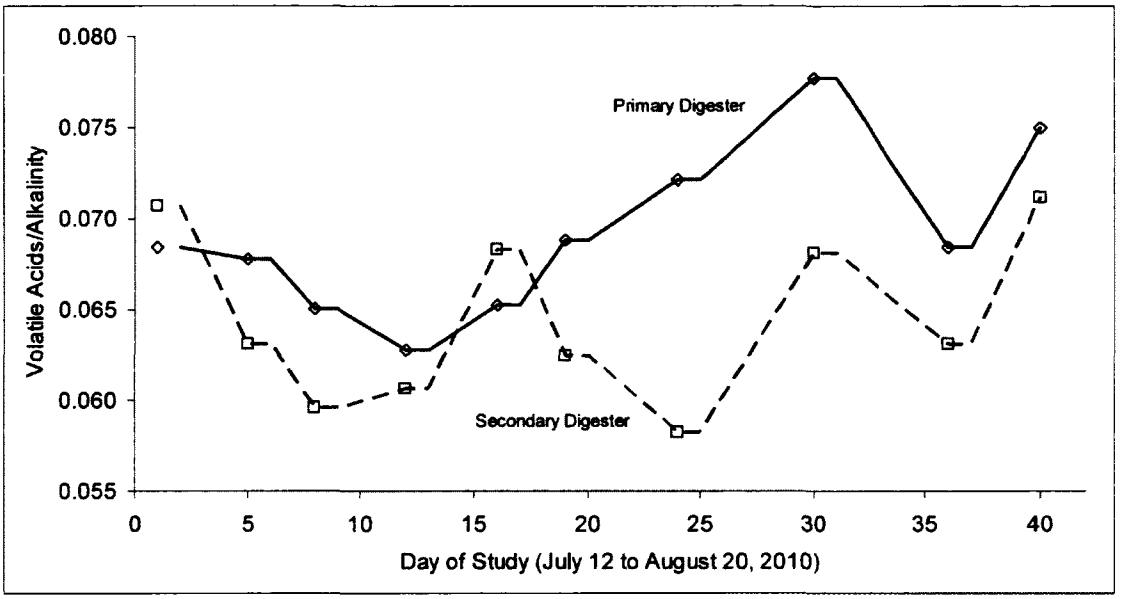

Figure 2.6 First and second stage digester sludge volatile acids/alkalinity ratio.

2.4.4 Operation and maintenance

The only mechanical problem that arose was the clogging of the hose that ran from the chopper pump to the sludge recirculation line. FVW often plugged this line. It then had to be manually cleared. Increasing the pump chopping time, decreasing the amount of waste added per batch, as well as increasing the rinse cycle may have decreased clogging. Overall there were no other mechanical problems with pumps or clogging downstream from the waste addition. Edelmann et al. (2000) also found no negative impact on mechanical operation of anaerobic digesters at a sewage treatment plant treating similar amounts of supermarket waste. The authors did however notice accumulation of fibrous scum build-up near the floating roof of the digester. This was not noticeable at the LWWTP, most likely because the digester in this study was much larger in volume (2986 m^3 compared to 240 m^3) and the study period was much shorter (6 weeks compared to 14 months).

2.4.5 Biosolids quality

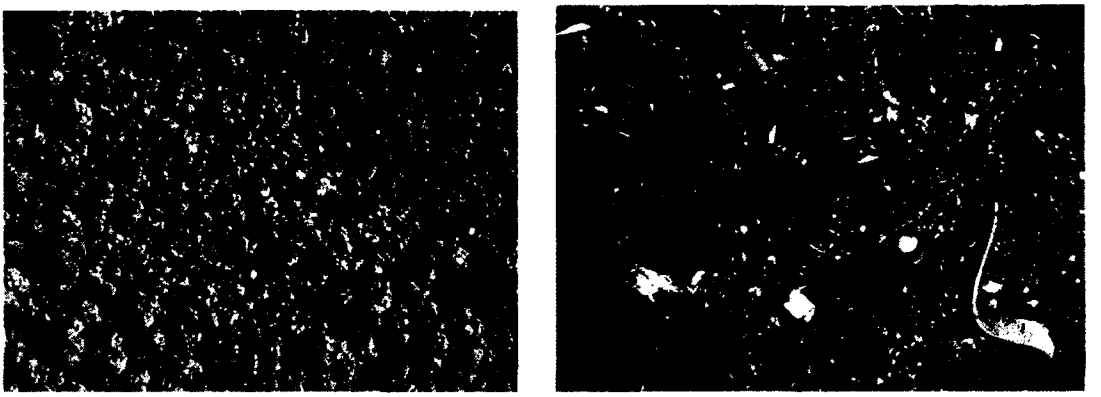

Figure 2.7 *Left-* Pre experiment biosolids *Right-* Biosolids centrifuged during the course of the experiment.

Biosolids collected during the study period were visibly higher in impurities such as elastic bands, "twist ties", and other plastic (Figure 2.7). The British Columbia Ministry of Environment Land Application Guidelines for the Organic Matter Recycling Regulation and Soil Amendment Code of Practice (2008) suggest no more than 1% foreign material in biosolids used for land application. Increased addition of FVW may cause regulatory problems with land application. A more thorough pre-treatment process may be necessary to reduce the impurities. Visible undigested organic matter, possibly corn husks, was also found in dewatered sludge. This undigested matter suggests that some of the added waste passed through the second stage digester without fully decomposing. Addition of waste to the first stage digester may have improved the digestion of more difficult to digest components by increasing the hydraulic retention time and preventing "short-circuiting" of waste when sludge was removed for centrifugation.

2.5 Conclusions

- FVW is a consistent, reliable, and clean organic waste stream.

- FVW can be disposed of in a fully operational WWTP with no digester disruption.
- FVW contributed to an increase in biogas production.
- Co-digestion may have been more complete if FVW was inserted into the first stage digester instead of the second.
- Anaerobic co-digestion of FVW with sewage sludge is a possible alternative to landfilling.

2.6 Acknowledgements

The authors wish to recognize the City of Prince George for their support. The following grocery stores, namely; Save-On Foods, Shoppers Wholesale Cash and Carry, Old Town Country Market were very generous for supplying the fruit and vegetable waste. The authors would also like to thank to Fikre Debela, Stacey Shantz, Gord Everitt, Tyler Olsen, and Joanne Logie for their assistance. This research was funded by the National Science and Engineering Research Council (NSERC) of Canada.

Preface

Chapter 3 of this thesis is a version of the manuscript that has been accepted for publication:

Park, N.D. Thring, R.W. Helle, S.S. 2011. Comparison of methane production co-digesting fruit and vegetable waste with first stage and second stage anaerobic digester sludge from a two stage digester. Accepted for publication in: *Water Science and Technology.* Manuscript number WST-WSTWS-EM111060

CHAPTER 3: Comparison of methane production co-digesting fruit and vegetable waste with first stage and second stage anaerobic digester sludge from a two stage digester.

3.1 Abstract

Fruit and vegetable waste (FVW) was co-digested with first stage sludge (FSS) and second stage anaerobic digester sludge (SSS) separately, over the course of ten days, in batch reactors. Addition of FVW significantly increased the methane production in both sludges. After 10 days of digestion FSS + FVW produced 514 ± 57 L CH_4 $kgVS^{-1}_{added}$ compared to 392 ± 16 L CH_4 $kgVS^{-1}_{added}$ for the SSS + FVW. The increased methane yield was most likely due to the higher inoculum substrate ratio of the FSS. The final VS and COD content of the sewage sludge and FVW mixtures was not significantly different from the control values, suggesting that all of the FVW added was degraded within 10 days. It is recommended that FVW be added to the first stage of the anaerobic digester in order to maximize methane generation.

3.2 Introduction

Anaerobic digestion is the decomposition of organic waste, by microorganisms, in an anoxic environment. A mixture of gases, containing mainly carbon dioxide and methane, are produced and collectively termed biogas. Often, wastewater treatment plants utilize anaerobic digestion to reduce the volume of sludge solids. As an added benefit, biogas produced can be consumed as fuel to offset the energy requirements of the wastewater treatment plant. Some of the advantages of using anaerobic digestion to treat the organic solids in wastewater include:

- low sludge volume compared to aerobic digestion
- low odour emissions

- stabilized digested matter can be used as a N and P rich fertilizer
- biogas produced is a renewable, carbon neutral source of energy

Due to the low solids content of municipal wastewaters, anaerobic digestion of low solids primary sludge often produces low volumes of biogas per unit of wastewater sludge treated. Addition of another organic waste stream, or co-digestion, can increase biogas production from low solids sludge. Co-digestion can improve biogas yield by: diluting toxic compounds, improving the balance of nutrients, increasing the synergistic effects of different microbial populations, and increasing the load of biodegradable matter in the digester (Sosnowski et al., 2003). Co-digestion of organic waste with sewage sludge in a fully functional wastewater treatment plant has been shown to improve biogas yields from anaerobic digesters (Zupancic et al., 2008; Bolzonella et al., 2006; Edelmann et al., 2000). Biogas production can be increased substantially, with little or no impact on the wastewater treatment plant effluent quality, and with low initial capital investment (Zupancic et al., 2008).

Food waste is a particularly promising substrate for anaerobic digestion due to its high nutrient content, high water content, and rapid degradability (Zhang et al., 2007). Food waste is also available in consistently large quantities. Statistics Canada (2009) estimates that 40% of the food that is produced in Canada ends up composted or in the landfill. This amounts to approximately 27 billion dollars of waste, or by comparison, slightly below the value of all Canadian agricultural and agri-food exports in 2007 (Gooch et al., 2010). The majority of this waste was disposed in landfills where it was allowed to decompose uncontrolled. Preserving landfill space, preventing groundwater contamination, and reducing greenhouse gas emissions can be achieved by diverting

organic waste from landfills. To circumvent the need for extensive sorting of residential waste, and to improve collection efficiency, fruit and vegetable waste (FVW) can be collected from direct sources such as supermarkets, wholesale distributors, and food processors. FVW often has a higher methane yield than other sources of organic waste such as yard wastes, paper, and mechanically sorted municipal solid waste due to its high VS content and water content (Ward et al., 2008). Specifically, Zhang et al. (2007) have shown mixed food wastes produce 435 L CH_4 $kgVS^{-1}_{removed}$. Gunaseelan (2004) has also extensively studied the methane production potential of over 54 various fruit and vegetable wastes using batch tests. Methane production ranged from 190-400 L CH_4 $kgVS^{-1}_{added}$.

There are often two anaerobic digesters in series at a wastewater treatment plant. As the first stage digester is filled with incoming sludge it drains into a second digester. Sludge is then periodically pumped from the second stage digester for dewatering. Having two digesters in series minimizes the shock associated with dewatering sludge, reduces short circuiting of fresh sludge, and allows for a backup digester in case of mechanical problems. Due to the longer retention time of the sludge in the second stage digester it is often lower in TS and VS than the primary stage sludge. Very little waste decomposition and biogas production occur in the second stage digester compared to the first (Appels et al., 2008). When co-digesting organic waste, waste can be pumped directly into either the first or second stage of the anaerobic sludge digester.

In a recent full scale study, Park et al. (2011) demonstrated increased biogas production when co-digesting FVW in the second stage of an anaerobic digester in a fully operational wastewater treatment plant.

In the present study, co-digestion of FVW with first stage digester sludge (FSS) and second stage digester sludge (SSS) was investigated to determine the appropriate digester for co-digesting FVW with sewage sludge. First stage and second stage sludge were collected from the Lansdowne wastewater treatment plant (LWWTP), in Prince George, British Columbia. The ability of each type of sludge to digest FVW was based on methane production, solids reduction, and chemical oxygen demand (COD) reduction.

3.3 Materials and Methods

3.3.1 Lansdowne Wastewater Treatment Plant

Please refer to section 2.3.1 for a detailed description of the LWWTP.

3.3.2 Food waste

Food waste used in this study was sampled from a 240 kg load of supermarket FVW collected from local supermarket outlets. Five to ten kilograms of FVW were selected by random shovelfuls and combined. Approximately 1 kg of roughly chopped FVW was blended to a thick consistency (2-3 minutes) using a Krups™ household blender. 100 g was frozen until use in batch digestion experiments. The FVW was tested for TS and VS by standard methods (APHA, 1998). pH was determined by centrifuging food waste at 6,000 r.p.m. for 10 minutes and measuring the pH of centrate using a Thermo Scientific Orion 3 Star™ pH meter. Food waste was also diluted 25:1 with deionised water, blended using a household blender for 10 minutes, and analyzed for chemical oxygen demand (COD) by the Hach™ method 8000 (Hach, 2010). Total volatile acidity and alkalinity were determined on the centrate of fresh waste, after centrifuging at 6,000 r.p.m. for 10 minutes, in duplicate, by the method outlined by Dilallo and Alberton (1961).

3.3.3 Sewage sludge

Approximately 2 L of FSS and SSS were sampled by wastewater treatment plant personnel for use in batch experiments. TS and VS of first and second stage sludge were determined in duplicate by standard methods (APHA, 1998). First and second stage digester sludge were diluted 2:1 with deionised water and analyzed for COD by the Hach method 8000 (Hach, 2010). Average plant values for pH, total volatile acidity, and alkalinity of sewage sludge were determined on non-centrifuged sludge by laboratory personnel as described in, "Food waste" above.

Table 3.0 Initial characteristics of FVW and sewage sludge collected from the first (FSS) and second stage (SSS) digester used in batch experiments.

Parameter	FVW	FSS	SSS
TS (%)	9.16 (0.63)	1.63 (0.01)	0.98 (0.01)
VS (%)	8.13 (0.26)	1.12 (0.01)	0.66 (0.01)
FS (%)	1.04 (0.66)	0.52 (0.00)	0.33 (0.00)
MC (%)	90.9 (0.6)	98.4 (0.01)	99.0 (0.01)
VS/TS (%)	89 (6)	68 (0.4)	67 (0.5)
COD (g O_2 L^{-1})	80 (6)	12.56 (0.03)	7.94 (0.48)
pH	4.6 (0.01)	7.1 (0.04)	7.1 (0.04)
Total Volatile Acidity (mg L^{-1})	1770 (42)	207 (20)	191 (14)
Total Alkalinity (mg $CaCO_3$ L^{-1})	770 (183)	3000 (9)	3021 (23)

3.3.4 Batch digestions

250 mL amber glass bottles were filled with 150 mL of either first or second stage digester sludge. Digester sludge received approximately 1 mL of deionised water as a control and co-digested sludges each received 1.0 g of FVW. Bottles were capped with rubber septa and the headspace was purged with nitrogen for 2 minutes. Bottle headspace pressure was equalized using an airtight syringe. Samples were then placed in a dark, reciprocating water bath at 36 °C, and shaked at 80 r.p.m. All samples were repeated in triplicate. Biogas volumes were measured by inserting an airtight syringe and allowing

the plunger to equilibrate. Daily room temperature and pressure at the time of gas sampling were recorded and gas volumes were corrected to STP (0 °C and 1 atm). A syringe was used to sample 0.1 mL of biogas to determine methane and carbon dioxide concentrations by gas chromatography. At the end of the experiment, samples of sludge were analyzed for TS and VS by standard methods (APHA, 1998) and COD by the Hach method 8000 (Hach, 2010).

3.3.5 Biogas analysis

0.1 mL samples of biogas were manually injected and analyzed for carbon dioxide and methane content using a SRI 8610C gas chromatograph equipped with a Haysep-D column and thermal conductivity detector (TCD). Helium at 15 mL min^{-1} was used as a carrier gas. Column oven temperature was set at 65 °C and the TCD oven at 104°C. Samples were injected at room temperature. A standard gas sample of methane and carbon dioxide was used to identify retention factors of component gases (Appendix B). Peak areas were corrected for differences in TCD response as outlined by Dietz (1967). Corrected peak areas were normalized to calculate gas volume in percent (Dietz, 1967).

3.3.6 Statistical data treatment

Average final VS, COD, biogas production, and methane production were analyzed by analysis of variance (ANOVA). When p was significant (< 0.05), statistical differences between treatment means were determined using the Tukey-HSD test. JMP 8 statistical software (SAS, NC, USA 2010) was used to perform statistical calculations. Microsoft Excel was used to produce graphs.

3.4 Results and Discussion

3.4.1 Initial characteristics of sewage sludge and FVW

The high water content and the high VS/TS ratio of FVW, shown in Table 3.0, suggest that it is well suited for anaerobic digestion (Zhang et al., 2007). TS, VS, and COD content of the FSS were considerably higher than the SSS as seen in Table 3.0. The FVW had a much higher TS, VS, and COD content than both of the sludges due to its higher solids content and relative freshness. FVW characteristics were consistent with those reported in the literature (Bouallagui et al., 2005). The neutral pH of both sludges is due to the high alkalinity and subsequent buffering capacity of the sludge. The high total volatile acidity of the FVW, and lack of buffering capacity, causes the pH to be lower than that of the sludges.

3.4.2 Biogas Generation

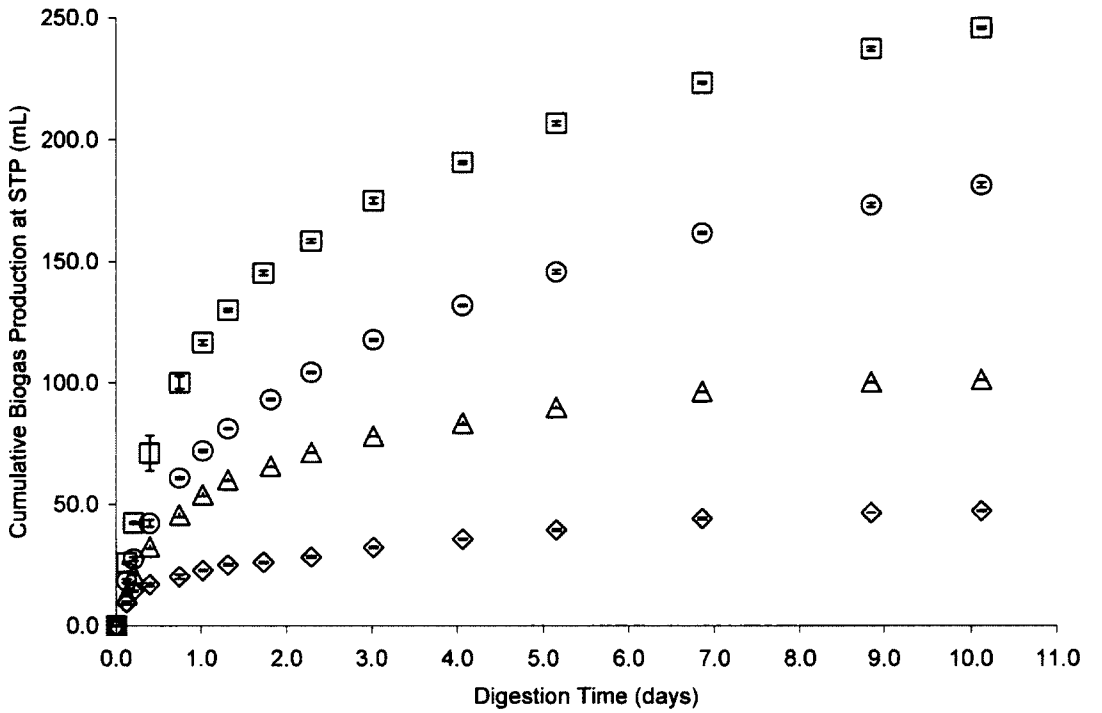

Figure 3.0 Cumulative biogas production at STP. □ FSS + FVW. ○ FSS control. Δ SSS + FVW. ◊ SSS control. Error bars represent the standard deviation of three measurements of the daily biogas generation.

Cumulative biogas generation was higher for the FSS than the SSS due to the higher initial VS content of the FSS (Figure 3.0). Average biogas yield per kg of $VS_{Consumed}$ was about the same for the FSS + FVW when compared to the SSS + FVW, 483 ± 33 and 492 ± 63 L $kgVS^{-1}_{consumed}$ (Table 3.1), respectively. Initial rates of biogas and methane production were determined by calculating the slope of a straight line fit to the first four data points (Table 3.1). The data fit a straight line well as seen by the R^2 values close to 1. Addition of FVW almost doubled the initial rate of biogas production in both cases. Initial rates of biogas production increased more in the FSS than the SSS

when compared to the controls. At the end of the digestion period the amount of VS consumed was greater for the FSS than the SSS. The SSS has been in the digesters for a longer period of time and therefore only the more difficult to digest components remain. Thus, VS destruction is less than what is seen in the FSS (Table 3.1). The final VS content of both sludges with FVW added was found to be statistically the same as the controls suggesting that all of the FVW was consumed within 10 days.

Table 3.1 Biogas and methane production rates between the SSS and PSS. Standard deviations are in parenthesis. Means with different letters indicate significant differences ($p < 0.05$).

Parameter	FSS	FSS + FVW	SSS	SSS + FVW
VS FVW added (g)	0	0.081 (0.001)a	0	0.082 (0.002)a
Initial VS (g)	1.661 (0.018)	1.741 (0.001)	0.981 (0.012)	1.063 (0.002)
Final VS (g)	1.230 (0.023)a	1.231 (0.015)a	0.816 (0.008)b	0.855 (0.03)b
$VS_{Consumed}$ (g)	0.432 (0.023)a	0.510 (0.015)b	0.164 (0.091)c	0.208 (0.027)d
Biogas Produced (mL)	181 (5)a	246 (16)b	47 (1)c	101 (2)d
Biogas $kgVS^{-1}_{consumed}$ (L)	420 (23)a	483 (33)a	287 (11)b	492 (63)a
Initial Rate (mL d^{-1})	105	179	42	82
R^2	0.97	0.99	0.86	0.98
CH_4 Produced (mL)	105 (4)a	147 (9)b	14.2 (0.4)c	47 (1)d
CH_4 $kgVS^{-1}_{consumed}$ (L)	244 (15)ab	289 (18)a	87 (4)c	226 (27)b
Net CH_4 (mL)	NA	42 (4)a	NA	32 (1)b
CH_4 $kgVS^{-1}_{added}$ (L)		514 (57)a		392 (16)b
Initial Rate (mL d^{-1})	47	97	3.8	24
R^2	0.99	0.99	0.97	0.99

3.4.3 Methane generation

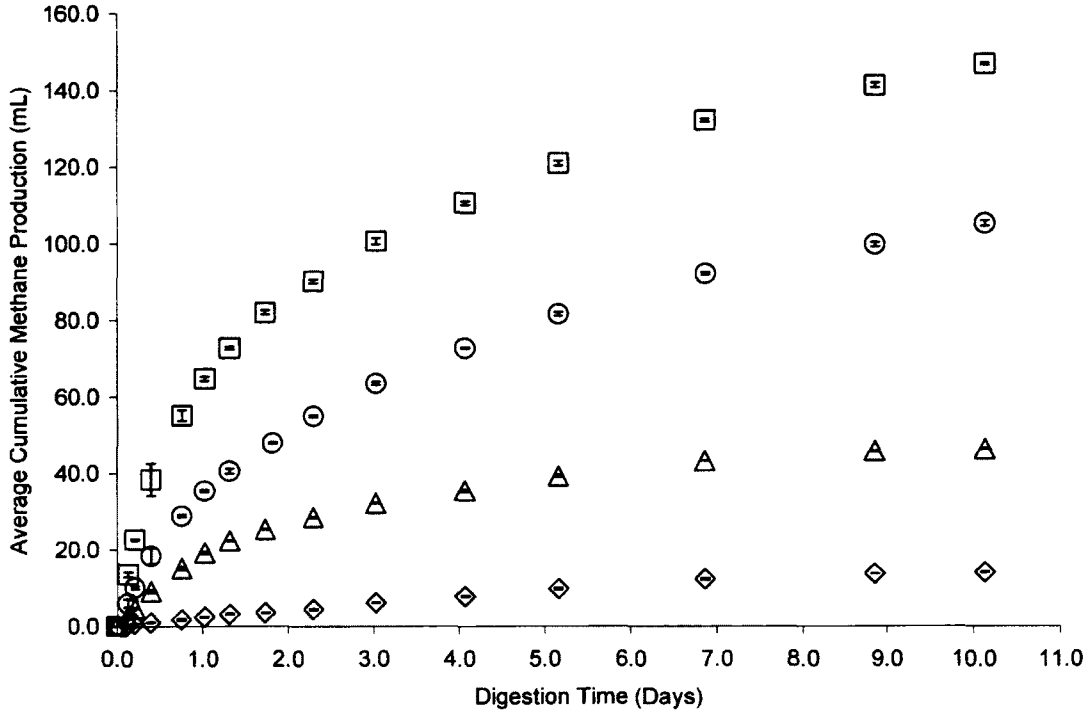

Figure 3.1 Cumulative methane production for: □ FSS + FVW. ○ FSS control. Δ SSS + FVW. ◊ SSS control. Error bars represent the standard deviation of three measurements of the daily biogas generation. All gas volumes were corrected to STP.

Cumulative methane generation was statistically higher when FVW was added to both the FSS and SSS as seen in Figure 3.1. Average net methane production was considerably higher (approximately 30%) in FSS (42 ± 4 mL) than in SSS (32 ± 1 mL). As seen in Table 3.1, the average volume of methane produced per gram of VS_{added} was significantly higher in the FSS than the SSS, 541 ± 57 L compared to 392 ± 16 L. These values where higher than the values reported by Zhang et al. (2007) who determined a methane generation rate of 348 L $kgVS^{-1}_{added}$, after 10 days, when digesting food waste. The FVW used in this study had a slightly higher VS/TS ratio. The added high quality VS of the FVW can account for the increase in methane production over the controls.

Methane production per kg of $VS_{consumed}$ of the FSS + FVW was significantly greater than that of the SSS + FVW (Table 3.1). In the second stage digester, of a two stage anaerobic digestion system, very little solids reduction and gas production occur (Appels et al., 2008). Thus, the microbial populations and subsequent inoculum substrate ratios (ISR's) are much lower in the second stage of the digester than the first (approximately 21:1 for FSS and 13:1 for SSS on a VS basis). It should be noted that these ratios do not represent true ISR's because inoculum sludge has not been completely "degassed" and therefore some of the VS may be in the form of primary wastewater solids. Increasing the ISR, to a point, has been shown to improve the specific methane yield in batch tests (Kameswari et al., 2011; Raposo et al., 2009). When the loading rate is increased by the addition of FVW the acidogenic bacteria increase carbon dioxide, acetate, and hydrogen production. The high carbon dioxide concentration of the SSS + FVW biogas (Figure 3.2) when compared to the FSS +FVW is a result of this. The methanogenic bacteria cannot increase their activity as quickly as the acidogens due to their long regeneration rate (15-16 days) when compared to the faster growing acidogens (< 24-90 hrs) (Deublin and Steinhauser, 2008). Therefore, when FVW is co-digested with sewage sludge, methane generation is dependant on the growth rate of the Methanogens (Bouallagui et. al., 2005).

3.4.4 Methane content of biogas

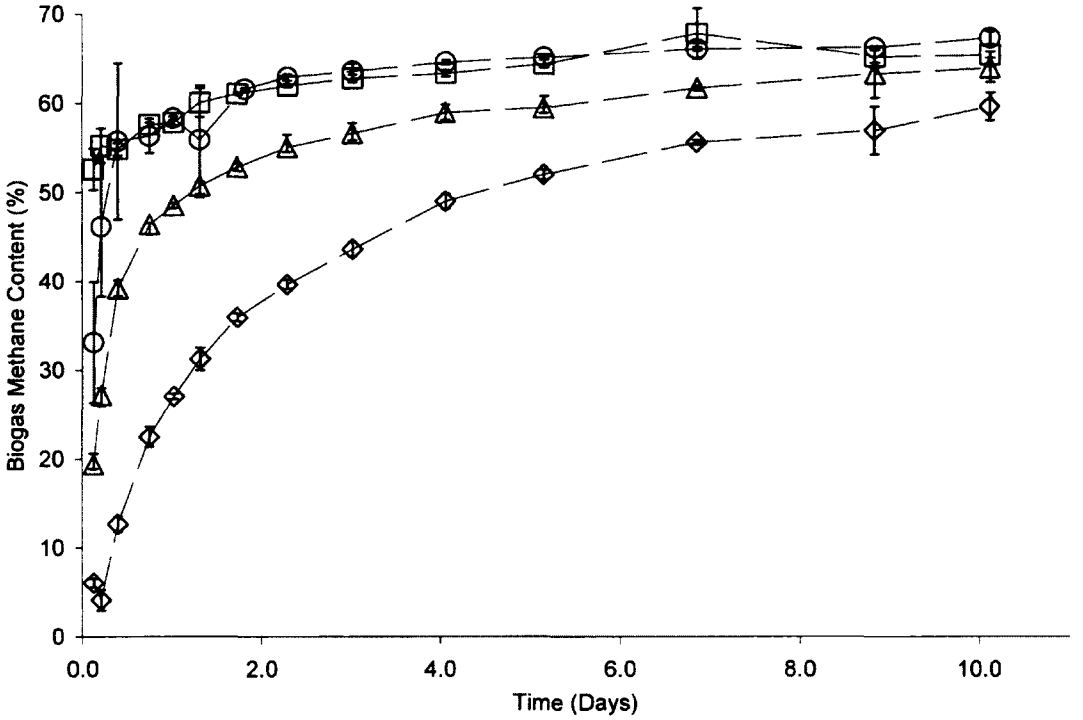

Figure 3.2 Biogas methane concentration of: □ PSS + FVW. ○ PSS control. Δ SSS + FVW. ◊ SSS control. Error bars represent the standard deviation of three measurements.

Methane content of the biogas increased as digestion time increased (Figure 3.2). Maximum methane content of the biogas was approximately 60-65%. Chen et al. (2010) found biogas produced from cafeteria waste and commercial kitchen waste to have similar methane content, 55 and 60% respectively. FSS reached maximum methane potential much faster than SSS. Final biogas methane concentrations were increased in both FVW amended sludges.

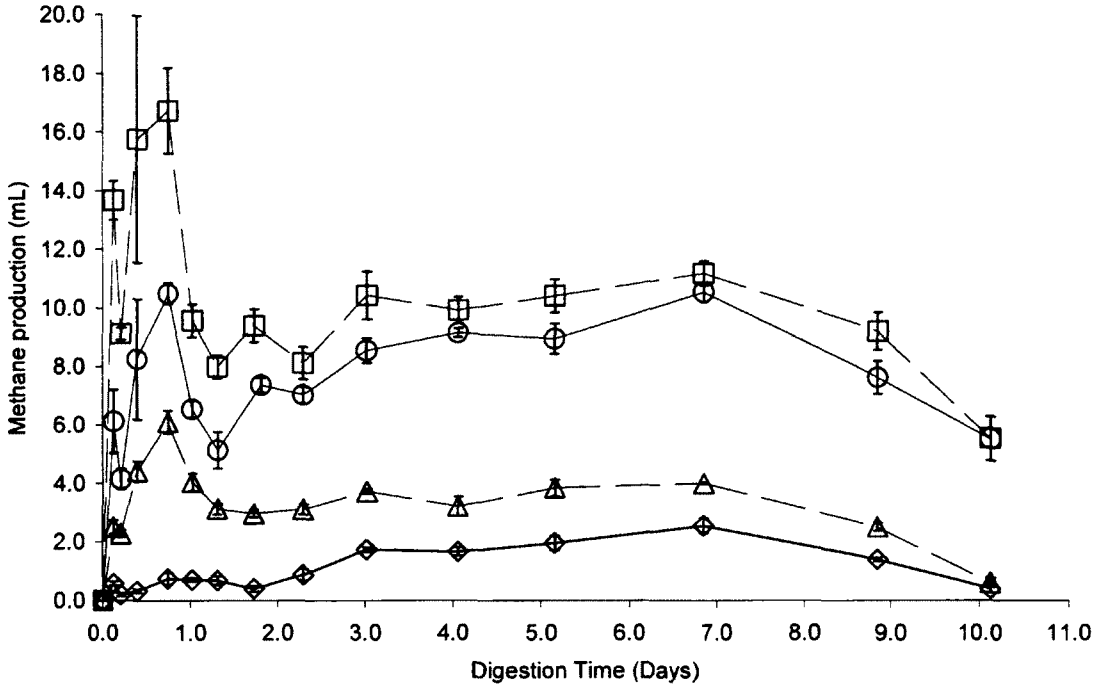

Figure 3.3 Daily methane production rate of sludges. □ FSS + FVW. ○ FSS control. Δ SSS + FVW. ◊ SSS control. Error bars represent the standard deviation of three measurements of the daily methane generation.

Daily methane generation reached a sharp maximum by approximately day 1 of the digestion (Figure 3.3). It then decreased as more difficult to degrade components were hydrolysed. Methane generation started to decline after day seven. Addition of FVW increased the daily methane production in both sludge's when compared to the controls. Initial daily methane generation was increased dramatically in both sludges amended with FVW suggesting that the majority of the FVW was very easily digested within the first 24 - 48 h.

3.4.5 COD reduction

Table 3.2 COD reduction of sewage sludge over 10 days of digestion. Standard deviations of three measurements are in parenthesis. Means with different letters indicate significant differences ($p < 0.05$).

Parameter	FSS ($g\ O_2\ L^{-1}$)	FSS + FVW ($g\ O_2\ L^{-1}$)	SSS ($g\ O_2\ L^{-1}$)	SSS + FVW ($g\ O_2\ L^{-1}$)
Day 1 COD	12.6 (0.3)a	12.6 (0.00)a	7.9 (0.5)b	8.0 (0.5)b
Day 10 COD	10.9 (0.1)a	10.7 (0.2)a	7.0 (0.3)b	6.6 (0.2)b
$CH_4\ COD^{-1}$($L\ gO_2^{-1}$)	65 (1)a	78 (12)a	17 (5)b	32 (5)b

Final COD values (Table 3.2) for the FSS were not significantly different than FSS + FVW. This suggests that all of the FVW added was removed within 10 days. SSS + FVW showed a slight decrease in the final COD values when compared to the control suggesting that FVW may have stimulated the digestion of sludge. Methane production per kg of $COD_{consumed}$ was higher in both of the sludges with co-digestate added. As seen in Table 3.2, FSS produced more than twice the amount of methane per kg of $COD_{consumed}$ than SSS.

3.5 Conclusions

The addition of FVW significantly increased the methane production of first and second stage digester sludge. However, the specific methane production of the FSS (514 ± 57 L CH_4 $kgVS^{-1}_{added}$) was significantly greater than that of the SSS (392 ± 16 L CH_4 $kgVS^{-1}_{added}$) most likely due to the higher ISR of the FSS. Post digestion COD and VS levels concluded that all of the FVW added was consumed within 10 days. When co-digesting fruit and vegetable waste with sewage sludge co-digestate should be added to first stage of the anaerobic sludge digester in order to maximize methane generation.

3.6 Acknowledgements

The authors wish to recognize the City of Prince George for their support. The authors would also like to thank Joanne Logie and Randy Garton, from the City of Prince George, for their assistance. This research was funded by the National Science and Engineering Research Council (NSERC) of Canada.

Preface

Chapter 4 of this thesis is a version of the manuscript under review:

Park, N.D., Thring, R.W., Helle, S.S., 2011. Combined alkaline and ultrasound pre-treatment of thickened pulp mill waste activated sludge for improved anaerobic digestion *Submitted to Biomass and Bioenergy.*

CHAPTER 4: Combined alkaline and ultrasound pre-treatment of thickened pulp mill waste activated sludge for improved anaerobic digestion

4.1 Abstract

Samples of pulp mill waste activated sludge were thickened by centrifugation, from 2.5 to 6.5%, and subjected to combined alkaline (20.6 and 26.1g NaOH $100gTS^{-1}$, respectively) and ultrasonic (39560 and 16822 kJ kg^{-1}, respectively) pre-treatment in order to improve methane production and shorten sludge retention time. Pre-treatment increased the soluble TS, VS, and COD of the pulp sludge 3-14 times over non-treated sludge. Batch anaerobic digestions, over 28 d, were used to compare the effects of sludge pre-treatment. Pre-treatment did not significantly improve biogas production over 28 d, but did increase the VS destruction (21 ± 3 to 30 ± 0.8% for 2.5% TS sludge and 23 ± 0.5 to 27 ± 0.7% for 6.5% TS sludge). Pre-treatment increased the initial rate of methane production. 80% of the total methane production was reached 5-6 days earlier when pre-treated. Overall methane production was found to be 404 ± 205 and 222 ± 123 L $kgVS^{-1}_{consumed}$ for 2.5% TS sludge non-treated and pre-treated sludge and 384 ± 183 and 354 ± 93 for 6.5% TS non-treated and pre-treated sludge, respectively. Pre-treatment reduced the dewaterability of both sludges. Thickening by centrifugation reduced the total S content of the sludge. Overall, biogas production from pulp sludge was unstable and inconsistent. Further research is required to determine the cause of inhibition.

4.2 Introduction

The production of wood pulp for paper manufacturing uses large amounts of water. Depending on the type of paper being made anywhere from 20 - 60 m^3 of water may be used to produce one tonne of paper (Thompson et al., 2001). Pulp and paper

effluents are mostly treated at the primary and secondary treatment levels. Primary treatment involves the sedimentation of fines, fibers and fillers that remain in the water due to poor separation during the pulping process (Mahmood and Elliot, 2006). Wood fiber found in the primary sludge is often recycled within the pulping process to increase yields, reduce costs, and reduce sludge production. Secondary sludge consists mainly of cell mass produced by the biological conversion of the soluble organic fraction of wastewater into carbon dioxide and water. Disposal of secondary sludge is more costly due to its poor dewaterability compared to primary sludge (Mahmood and Elliot, 2006). The production of secondary sludge has been on the rise in recent years as pulp production increases and as environmental regulations pertaining to effluent quality have become more stringent (Mahmood and Elliot, 2006). Sludge disposal and management can amount to 60% of the total cost of pulp mill wastewater treatment; for this reason the minimization of sludge production is important (Canales et al., 1994).

One method that is often used to reduce the volume of municipal wastewater sludge is anaerobic digestion (AD). Anaerobic digestion is the biological breakdown of organic waste in the absence of oxygen. The process of AD is often broken down into four general steps; hydrolysis, acidogenesis, acetogenesis, and methanogenesis. During the hydrolysis stage large, insoluble polymers are broken down into soluble monomers by extra-cellular enzymes. These monomers are then converted into short chain organic acids by the acidogenic bacteria. Next, the organic acids are then converted to acetate by the acetogenic bacteria. Lastly, methanogenic microorganisms convert acetate, carbon dioxide, and methyl type substrates into methane. Some of the benefits of anaerobic digestion include; reduced sludge volume, sludge stabilization, sludge disinfection, and

energy recovery in the form of methane. Compared to the use of AD in municipal wastewater sludge treatment, the utilization of AD in the pulp and paper industry is less widespread. There have only been four anaerobic treatment system utilized in Canada for the treatment of pulp and paper sludge (Elliot and Mahmood, 2007). Of these four installations only two are currently operational (Elliot and Mahmood, 2007). Sludge produced from the pulp and paper industry is mainly composed of microbial cell mass that forms during secondary treatment and lignin and chemical residuals from the pulping process (Kyllonen et al., 1988). This type of waste is less amenable to degradation than the primary wastewater solids that are anaerobically digested in the municipal sector. Consequently, the AD of pulp sludge requires long retention times, has a low degradation efficiency, and poor economics. Therefore, AD is less widely used in the pulp and paper industry (Elliot and Mahmood, 2007; Lin et al., 2009).

Increasing sludge digestion through sludge disintegration can increase methane production, decrease sludge volume, reduce sludge retention time, and thereby improve the overall economics of the process. Disintegration helps to speed up the hydrolysis stage by mechanically, chemically, thermally, or biologically aiding in the breakdown and solubilization of the sludge by reducing floc particle size and rupturing microbial cell walls.

Alkaline addition has been shown to increase solubilization of pulp and paper sludge and improve biogas yield (Lin, L., 2009; Heo et al., 2003). Sodium hydroxide is most often used over other chemicals such as KOH and $Ca(OH)_2$ due to its high rate of COD solubilization (Kim et al., 2003). Hydroxy anions weaken cell walls and break a part floc structure rendering the sludge amenable to further treatment. Alkaline pre-

treatment has been combined with ultrasound, microwave, thermal, high pressure gradients to further sludge breakdown (Yiying, et al., 2009; Dogan and Sanin, 2009; Neyens and Baeyens, 2003; Daniel et al., 2007).

Ultrasound pre-treatment of municipal wastewater sludge has been studied at length due to its ease of operation and effectiveness (Khanal et al., 2007). Ultrasound treatment involves using high frequency sound waves generated by a vibrating probe. As the sound waves travel through the liquid, gas bubbles are formed and collapse violently producing localized high temperatures and pressures. Cell walls and floc structures are destroyed making their contents' susceptible to anaerobic digestion. Combinations of both ultrasound and alkali pre-treatment have been shown to improve sludge digestion over either treatment alone (Chiu et al., 1997; Yiying et al., 2009). Improvement of sludge sonication efficiency has been improved by increasing the total solids content of the sludge (Wang et al, 2005; Khanal et al., 2006).

Much of the research conducted on the pre-treatment of secondary sludges has been done using municipal wastewater sludges. Much less has been reported on the treatment of sludges produced from pulp mill wastewater treatment (Elliot and Mahmood, 2007). Some studies pre-treating pulp sludge have been reported in the literature, however; few have reported combined treatment methods, or have pre-treated thickened pulp sludge (Yunquin et al., 2010; Lin et al., 2009; Wood et al., 2009).

The objective of this experiment was to determine the methane potential of secondary sludge produced by the Quesnel River Pulp (QRP) mill. Thickened (6.5% TS) and non- thickened sludges (2.4% TS) were subject to alkaline pre-treatment followed by ultrasonication in order to improve sludge AD efficiency and compared to non pre-treated

sludge. Pre-treatment effectiveness was analyzed by comparing the soluble COD (sCOD), soluble TS (sTS), and soluble VS (sVS) fraction in treated and non-treated sludges. AD efficiency was based on methane production and VS reduction. Hydrogen sulphide production was also calculated by comparing sludge sulphur content before and after digestion. QRP sludge is known to be high in S due to sulphite addition during the pulping process.

4.3 Materials and Methods

4.3.1 Pulp sludge

Secondary (WAS) sludge was collected from the Quesnel River Pulp mill, in Quesnel, B.C. Canada. The QRP mill produces bleached chemi-thermo-mechanical pulp (BCTMP) and thermo mechanical pulp (TMP). Wastewater is composed of approximately 2:1 BCTMP: TMP effluent. The plant typically uses 60% white spruce and 40% lodgepole pine. Wastewater is treated using a moving bed biological reactor followed by activated sludge treatment. Pulp mill sludge (PMS) samples were stored at 4 °C and used within 24 hrs of sampling.

4.3.2 Pre-treatment

Sludge was used at initial solids content and was thickened to approximately 6.5% TS by centrifugation at 6,000 rpm for 5 min. Non-thickened sludge was dosed with NaOH at 500 mg L^{-1} (20.6g NaOH $100g^{-1}$ TS) and thickened pulp sludge was dosed with NaOH at 1700 mg L^{-1} (26.1g NaOH $100g^{-1}$ TS). Samples were then mixed for 10 min using a Hamilton Beach™ handheld mixer, and allowed to sit for two hours. 400 mL portions of treated sludge were then sonicated using a 40 kHz Fisher Scientific™ model 150T ultrasonic dismembrator (150W maximum output). Sludge samples were packed in

ice to prevent overheating and sonicated for 2 hours, 10 s on 5 s off, for a total of 1.5 h, at 60% amplitude, with a 1/8" microtip titanium probe. Specific energy was defined as,

$$Es = (P)(t)/(v)(TS),$$

Where, P = ultrasonic power (W), t= ultrasonic time (s), v= sample volume (L), TS= total solids concentration (kg L^{-1}). Values were calculated to be 39560 kJ $kg^{-1}TS^{-1}$ for the 2.5% TS sample and 16822 kJ $kg^{-1}TS^{-1}$ for the 6.5% TS sample.

4.3.3 Sludge characterization

Approximately 15 L of pulp sludge was sampled for use in batch experiments. Sludge samples were characterized for TS and VS in duplicate by standard methods (APHA, 1998). COD was determined in triplicate on diluted sludge samples by the closed reflux method outlined by the Hach method 8000 (Hach, 2010). Sludge samples were centrifuged at 20,000 rpm for 10 min and decanted to determine the sTS, sVS, and sCOD. Supernant pH was determined using an Orion pH probe. Pulp sludge samples where dried at 104 °C for 48 h and analysed for total C, N, and S content using < 100-mesh samples (ground in a Model MM200 ball mill; Retsch, Haan, Germany) via dry combustion method in a Model 1500 Elemental Analyzer (Fisons, Milan, Italy).

4.3.4 Inoculum sludge

Inoculum sludge was collected from the first stage anaerobic digester at the Lansdowne wastewater treatment plant (LWWTP) in Prince George, B.C., Canada, for use as inoculum. Anaerobic digesters are fed semi-continuously with sludge from two primary clarifiers. The primary digester is operated at mesophilic (36 ± 1 °C) temperature. More information on the wastewater treatment process at the Lansdowne Wastewater Treatment Plant can be found in section 2.3.

4.3.5 Batch digestions

250 mL amber glass bottles were filled with 75 g of sludge inoculum and 75 g of pulp mill sludge. Control inoculum received 75 mL of deionised water. The experimental units are as follows; control, 6.5% non-treated PMS, 6.5% pre-treated PMS, 2.4% non-treated PMS, 2.4% pre-treated PMS. All digestions were repeated in triplicate. Bottles were capped with rubber septa and the headspace was purged with nitrogen for 2 min. Bottle headspace pressure was equalized using an airtight syringe. Samples were then placed in a dark, reciprocating water bath at 36 °C, and shaked at 80 r.p.m. Biogas volumes were measured by inserting an airtight syringe and allowing the plunger to equilibrate. Daily room temperature and pressure at the time of gas sampling were recorded and gas volumes corrected to STP (0 °C and 1 atm). A syringe was used to sample 0.1-0.2 mL of biogas to determine methane and carbon dioxide concentrations by gas chromatography. At the end of the experiment samples of sludge were analyzed for TS and VS by standard methods (APHA, 1998).

4.3.6 Biogas analysis

0.1-0.2 mL samples of biogas were manually injected and analyzed for carbon dioxide and methane content using a SRI 8610C gas chromatograph equipped with a Haysep-D column and thermal conductivity detector (TCD). Helium at 15 mL min^{-1} was used as a carrier gas. Column oven temperature was set at 65 °C and the TCD oven at 104 °C. Samples were injected at room temperature. A standard gas sample of methane and carbon dioxide was used to identify retention factors of component gases. Peak areas were corrected for differences in TCD response as outlined by Dietz (1967). Corrected peak areas were normalized to calculate gas volume in percent (Dietz, 1967).

4.3.7 Specific resistance to filtration

Specific resistance to filtration test (R) has been widely used to asses the filterability and the dewaterability of sludges. The test involves the use of a Buchner funnel, filter paper, and pressure or vacuum. The volume of filtrate is recorded with respect to time. In order to make the measured filterability of the sludge independent from as many variables as possible Coackley and Jones (1956) described a mathematical model that takes into account the sludge volume filtered, area of filter surface, the solids content of the sludge, and the filtration vacuum pressure. 100 mL of sludge, at 10 °C, was filtered using an 11 cm in diameter, Whatman #2 filter paper, at a constant vacuum pressure of 0.69 bar. Sludge was filtered for 32 minutes and the volume of filtrate collected was recorded with respect to time. R was calculated from a plot of filtration time/filtrate volume vs. filtrate volume as described in detail by Habiba et al. (2009).

4.3.8 Statistical data treatment

Average final TS, VS, biogas production, and methane production were analyzed by analysis of variance (ANOVA). When p was significant (< 0.05), statistical differences between treatment means were determined using the Tukey-HSD test. JMP 8 statistical software (SAS, NC, USA 2010) was used to perform statistical calculations. Microsoft Excel was used to produce graphs.

4.4 Results and Discussion

4.4.1 Effect of sludge pre-treatment

Table 4.0 Characteristics of thickened (6.5% TS), non-thickened (2.5%TS), and inoculum sludge pre-treated with NaOH and ultrasound. Numbers in brackets represent standard deviations, n=2).

Parameter	2.5% TS Non-treated	2.5% TS Pre-treated	6.5% TS Non-treated	6.5% TS Pre-treated	Inoculum
TS (%)	2.42 (0.01)	2.73 (0.02)	6.52 (0.06)	6.42 (0.01)	1.67 (0.03)
VS (%)	1.87 (0.01)	2.01 (0.01)	5.52 (0.07)	5.32 (0.01)	1.18 (0.03)
VS/TS (%)	77.0 (0.2)	73.8 (0.08)	84.7 (0.2)	82.8 (0.3)	70.7 (0.76)
FS (%)	0.56 (0.003)	0.71 (0.01)	0.99 (0.004)	1.1 (0.02)	0.49 (0.01)
MC (%)	97.58 (0.01)	97.27 (0.02)	93.48 (0.06)	93.58 (0.01)	98.33 (0.03)
COD (gO_2L^{-1})	29.8 (0.7)	27.4 (1.6)	87.8 (0.8)	75.0 (1.3)	16.9 (0.4)
sCOD/tCOD (%)	6 (1)	19 (2)	3.6 (0.2)	17.9 (0.5)	7.9 (0.3)
C:N Ratio	10.5:1	10.3:1	9.8:1	10.2:1	8.1:1
pH	7.3	8.4	7.2	8.8	7.3

As seen in Table 4.0, the VS/TS content of the pulp sludge's is high, even larger than the municipal primary sludge used as inoculum, suggesting that it is ideal for anaerobic digestion (Zhang et al., 2007). FS content of the pre-treated sludge increased due to the added NaOH during the pre-treatment process as well as a small amount of possible sludge mineralization caused by pre-treatment. Pre-treatment reduced the COD value of both sludges. This may have been due to loss of volatile components in the sludge during ultrasonication (Santos et al., 2009). Sludge solubilization (sCOD/tCOD) increased 3 times in the pre-treated 2.5%TS sludge and almost 5 times in the pre-treated 6.5% TS sludge. The pH of the pre-treated sludge supernant increased by just over 1 unit in both sludges due to the addition of NaOH. Saha et al. (2011) thoroughly analyzed secondary sludge from the QRP mill in 2010 and found the TS, VS, COD, and sCOD to be similar to what is reported in Table 4.0.

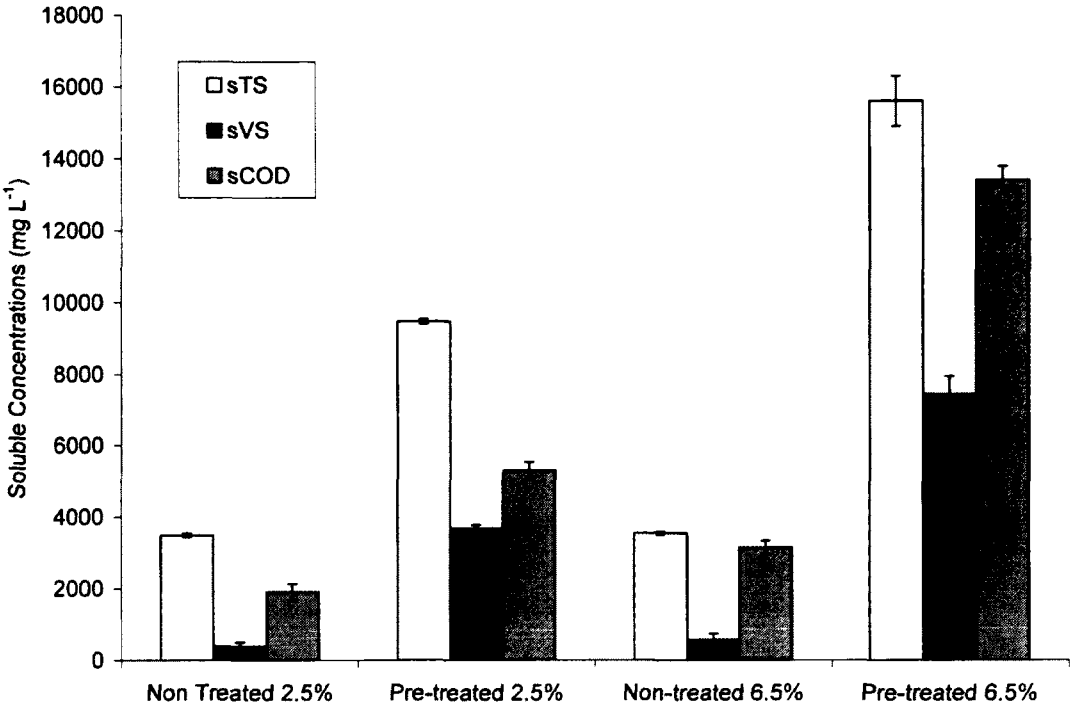

Figure 4.0 Difference in soluble TS, VS, and COD between pre-treated and non-treated sludge. Error bars represent the standard deviation of 2 (TS and VS), or 3 (COD) measurements.

Figure 4.0 shows the difference in the soluble TS, VS, and COD between the pre-treated and non-treated sludge. In the 2.5% TS PMS pre-treatment increased the sTS, sVS, and sCOD by approximately 3, 9, and 3 times, respectively. Pre-treatment of 6.5% TS PS increased the sTS, sVS, and sCOD by approximately 4, 13, and 4 times, respectively. The 6.5% TS sludge was dewatered by centrifugation prior to use. This would have lowered the initial soluble organic content of the sludge making effects of pre-treatment seem larger. Also, the 6.5% TS sludge was dosed with a higher concentration of NaOH (initial sludge tests indicated a TS content of 8.2% when centrifuged at 6000 rpm for 5 min, but the subsequent batch of sludge used in this test was more difficult to dewater). Pre-treatment of 6.5% TS sludge may have also improved

due to the increased ultrasound efficiency at higher TS contents (Khanal et al., 2006; Wang et al., 2006).

Wood et al. (2009) treated sulfite mill secondary sludge and Kraft mill secondary sludge with ultrasound at 20 kHz. COD solubilisation was low compared to other pre-treatment methods. Similarly to this study, the sulfite mill secondary sludge increased from 11% sCOD to 23% sCOD and the Kraft mill sludge increased from 1% to approximately 5% sCOD after pre-treatment. Saha et al. (2011) have also treated pulp mill secondary sludge originating from the QRP with ultrasound (at 20 kHz) alone and found sCOD increased with increasing treatment time. The sCOD/tCOD values were slightly higher than reported in this study. This may have been due to the higher ultrasound intensity at 20 kHz. Values increased from 5- 7.8 times over the control depending on the treatment time. Yunquin et al. (2009) treated a combination of primary and secondary pulp and paper sludge with lower dose (16gNaOH $100gTS^{-1}$) of NaOH for a longer time (6 hours). Soluble COD increased approximately 12 times when compared to the control. Soluble COD increases may have been higher due to the solubilization of primary sludge that was high in lignocellulosic residues.

4.4.2 Biogas Production

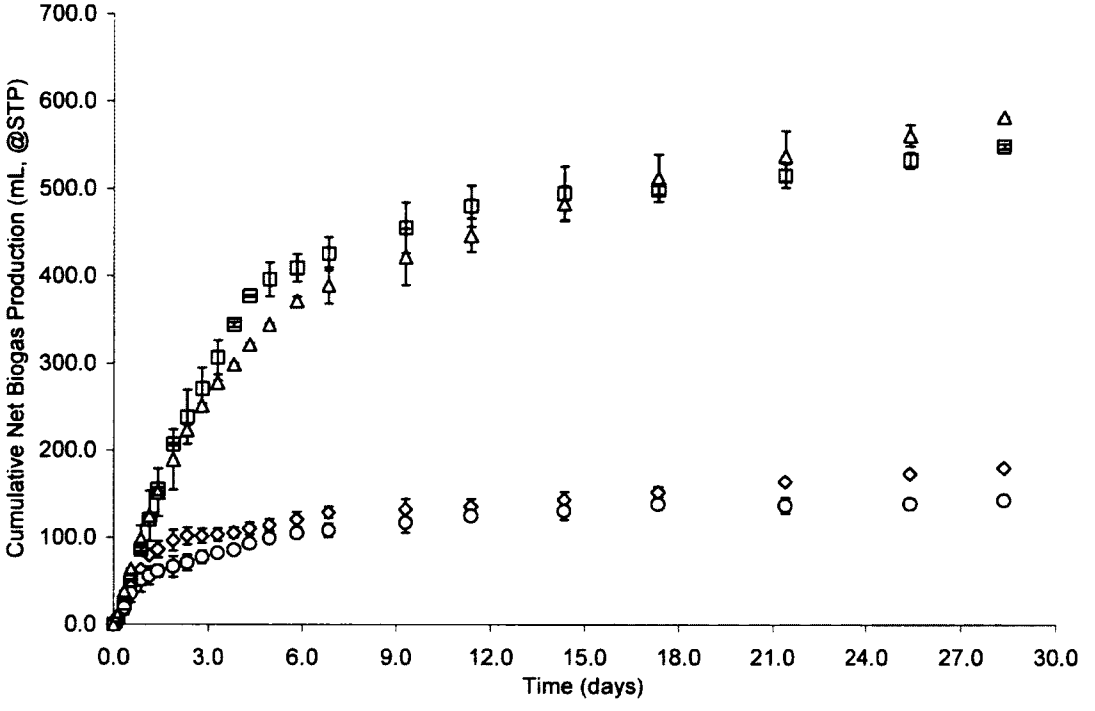

Figure 4.1 Net cumulative biogas generation. □ 6.5% pre-treated Δ 6.5% non-treated ○ 2.5% pre-treated ◊ 2.5% non-treated. Error bars represent the standard deviation of the daily biogas production from three replicates. Biogas generated from inoculum only blanks was subtracted from the data.

Initially, biogas production increased in the thickened sludge when compared to the non pre-treated thickened sludge (Figure 4.1). Around day 20 for the 6.5% TS sludge the cumulative biogas volume of the non-treated sludge surpassed the pre-treated sludge. After 28 d both of the non-treated sludges had produced more biogas than the pre-treated sludge (Figure 4.1). Statistically, pre-treatment of sludge did not increase biogas production over 28 days. Wood et al. (2009) also reported that pre-treatment with sonication did not significantly increase biogas yield in either Kraft or sulphite pulp mill sludges, yet an initial improvement in the rate of gas production was observed. 80% of the total biogas production was reached by day 8.5 for the pre-treated 2.5% TS sludge compared to day 14.5 for the non pre-treated 2.5% TS sludge (data not shown). This is an

increase of 6 days. For the 6.5% TS sludge, 80% of total biogas production was reached by day 8 for the pre-treated sludge compared to day 13 for the non pre-treated sludge (data not shown). This was an improvement of 5 days.

4.4.3 Methane Production

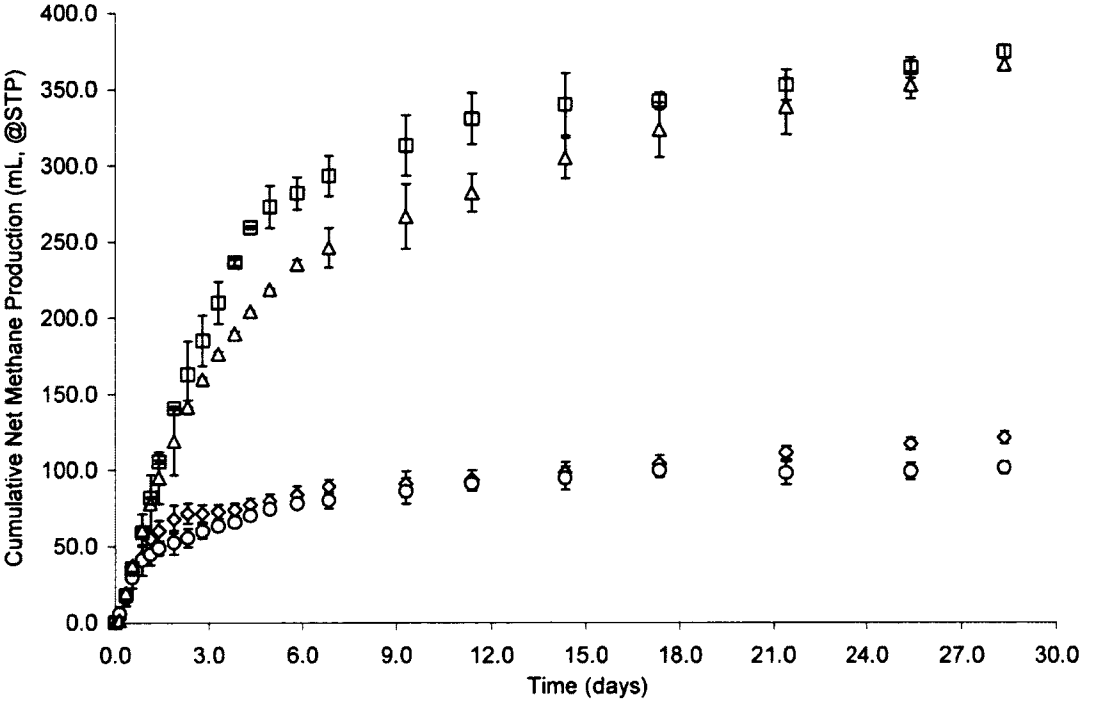

Figure 4.2 Net cumulative methane generation. □ 6.5% pre-treated Δ 6.5% non-treated ○ 2.5% pre-treated ◊ 2.5% non-treated. Error bars represent the standard deviation of the daily methane production from three replicates. Methane generated from inoculum only blanks was subtracted from the data.

Initially, methane production increased in the thickened sludge compared to the non-treated thickened sludge (Figure 4.2). On approximately day 23 for the 6.5% TS sludge the cumulative methane production of the non pre-treated sludge surpassed the pre-treated sludge. After 28 days both of the non-treated sludges had produced more methane than the pre-treated sludge (Figure 4.2). Pre-treatment did not significantly improve methane production. 80% of the total methane production was reached by

approximately day 7.5 for the pre-treated 2.5% TS sludge compared to day 14 for the non pre-treated 2.5% TS sludge (data not shown), an increase of 6.5 days. For the 6.5% TS sludge, 80% of total biogas production was reached by day 7.5 for the pre-treated sludge compared to day 13 for the non pre-treated sludge (data not shown). This was an improvement of 5.5 days. Karlsson et al. (2011) also reported very similar trends in methane production after pre-treating WAS, originating from two different pulp mills, with ultrasound. Initial methane production rates increased, but the effects were diminished over time (Karlsson et al., 2011).

Overall methane and biogas production decreased slightly when sludge was pre-treated. The results obtained by Wood et al. (2009) suggested that addition of NaOH may solubilize recalcitrant compounds, or generate inhibitory compounds thus lowering the methane yield. Mineralization of sludge components may have caused the slightly lower total methane output from the pre-treated sludge. As seen in Table 4.0, the FS content of both sludges increased, and the VS/TS ratio decreased after pre-treatment.

4.4.4 Post digestion sludge characteristics

Table 4.1 Sludge characteristics post anaerobic digestion. Values in brackets represent standard deviations, n=3.

Parameter	2.5% TS Non-treated	2.5% TS Pre-treated	6.5% TS Non-treated	6.5% TS Pre-treated
Initial VS (g)	1.397 (0.044)	1.511 (0.046)	4.142 (0.080)	3.990 (0.044)
Final VS (g)	1.108 (0.042) a	1.057 (0.012) a	3.189 (0.019) b	2.932 (0.029) c
VS Consumed (g)	0.290 (0.042) a	0.454 (0.012) b	0.952 (0.019) c	1.058 (0.029) d
VS reduction (%)	21 (3) a	30 (1) b	23 (1) ab	27 (1) bc
Net Biogas (ml)	180 (99) a	143 (90) a	582 (280) a	549 (153) a
Biogas $kgVS^{-1}_{Consumed}$ (L)	603 (299) a	313 (195) a	610 (290) a	518 (137) a
Net Methane (ml)	122 (69) a	102 (58) a	366 (176) a	375 (105) a
Methane $kgVS^{-1}_{Consumed}$ (L)	404 (205) a	222 (123) a	384 (183) a	354 (93) a
% CH_4 in Biogas	64-70	66-70	62-66	65-69
Final pH	7.4	7.5	7.5	7.6
R ($m\ kg^{-1}$)	5.61E+14	9.61E+14	7.91E+14	14.6E+14

The net $VS_{consumed}$ for pre-treated sludge's was significantly greater than non-treated sludge's (Table 4.1). This corresponded to a greater VS reduction efficiency in pre-treated sludge (Table 4.1). Improvements were similar to those reported by Saha et al. (2011) who at after 90 min of sonication, at 20 kHz, and 45 days of AD, using QRP sludge, improved VS reduction from 23 ± 3% to 30 ± 4%. Net production of biogas was statistically the same whether or not sludge was pre-treated (Table 4.1). Due to the higher VS destruction efficiency, biogas produced per g of VS was lower in the pre-treated sludge. Biogas production was 3 - 4 times greater in the 6.5% TS sludge than the 2.5% TS sludge due to the increased VS content of the thickened sludge. Net methane production was also the same and did not change with pre-treatment. Methane content of the biogas was slightly higher for pre-treated sludges. Methane production was consistent with the values reported (320 L CH_4 $kgVS^{-1}_{consumed}$) for batch digestions of pulp mill sludge (PMS), pre-treated with NaOH, by Lin et al. (2009). Puhakka (1992) reported similar values for biogas generation, 570 L biogas $kgVS^{-1}_{consumed}$, using a pilot scale reactor to digest Kraft pulp mill WAS.

It should be noted that overall biogas production was unstable (Appendix C). At least one batch digestion out of three (in some cases two) had a significantly lower biogas/methane production compared to the other two samples. This can bee seen in the high standard deviations reported for net methane and biogas production. More research is required to determine the cause of inhibition. One possibility is that sulphur reducing bacteria (SRB) may have out competed methane producing bacteria (MPB) in some of the batches. This would explain the increased VSD without an increase in methane production. Pre-treatment seemed to increase the amount of inhibition as seen in

Appendix C. Therefore, in the case of high sulphur waste streams pre-treatment not only benefits the MPB, but also the SRB. More research is needed to determine the conditions which favor MPB.

Final pH of supernant from digested sludge was found to be near the optimum range of 6.7-7.5 for methane-forming bacteria (Deublein and Steinhauser, 2008). This suggests that addition of sodium hydroxide did not adversely affect the AD process, nor was acidification by hydrogen sulphide a major concern.

Pre-treatment almost doubled the specific resistance to filtration of both the digested sludges as seen by the larger R values reported in Table 4.1. Saha et al. (2011) also reported a reduction of pre-digestion sludge dewaterability after ultrasonication.

4.4.5 Sulphur Reduction

Table 4.2 Sludge sulphur reduction.

Parameter	2.4% TS Non-treated	2.4% TS Pre-treated	6.5% TS Non-treated	6.5% TS Pre-treated	Inoculum
% S (total)	1.97 (0.02)	1.98 (0.03)	1.39 (0.02)	1.37 (0.02)	0.99 (0.02)
Initial S (mg batch^{-1})	52.7 (0.6)	48.3 (0.7)	79.0 (1.1)	79.1 (1.0)	12.3 (0.3)
Final S (mg batch^{-1})	40.5 (0.6)	30.3 (0.7)	67.4 (1.2)	68.8 (0.4)	10.8 (0.7)
Net Diff (mg batch^{-1})	10.8 (1.2)	16.6 (1.3)	10.2 (1.8)	8.9 (1.3)	1.46 (0.8)
H_2S Max (%)	4.0 (2.2)	7.7 (4.9)	1.2 (0.6)	1.1 (0.3)	0.7 (0.4)

Initial total sulphur content was lower in the thickened sludge than the non-thickened. This suggests that the majority of the sulphur is in soluble forms (most likely SO_4^{2-}) and dewatering by centrifugation decreases the sulphur content considerably. Pre-treatment had no discernable effect on the sulphur concentration of the sludge. Non-thickened sludge had increased sulphur consumption (Table 4.2) when compared to thickened sludge due to the overall higher soluble sulphur component. Maximum H_2S content was calculated by assuming that all net sulphur lost (initial S mg batch^{-1} – final S

mg batch^{-1} – inoculum sulphur lost mg batch^{-1}) was in the form of H_2S. This was not the case as some sulphur may have been liberated as other reduced sulphur compounds such as methylsulphide and dimethlysulphide. Therefore the values stated in Table 4.2 are high estimates. Standard deviations are also high due to the variability in biogas production. Hydrogen sulphide production from the thickened sludge was in the necessary range for proper operation, 0.5-6% (Chynoweth and Isaacson, 1987). Dufresne et al. (2001) reported excellent biogas production, and COD removal, anaerobically digesting Kraft pulp mill condensates at a biogas hydrogen sulphide concentration close to 4%. Non-thickened sludge was near the upper limit for H_2S headspace concentration suggesting that sludge thickening may be necessary to reduce the soluble sulphur component, and lower the H_2S content of the biogas in order to prevent problems with excessive H_2S production and possible inhibition.

4.4.6 Economics

Pre-treatment using a lab scale ultrasound device requires approximately 297 kWh m^{-3} for the 2.5% TS and 6.5% TS sludge each. At \$0.07 kWh^{-1} it would cost approximately \$21.00 m^{-3} for ultrasonic pre-treatment. Sodium hydroxide addition at \$350 Mg^{-1} would cost \$1.75 for the 2.5% TS sludge and \$5.95 for the 6.5% TS sludge per m^3 making the overall cost for pre-treatment \$22.75 m^{-3} (2.5% TS) and \$26.95 m^{-3} (6.5% TS) . Capital investment, ultrasound probe replacement (every 1.5 - 2 yrs), operational, and maintenance costs would also have to be considered. Also, decreased dewaterability would increase costs associated with dewatering and disposal. With no significant increase in methane production the cost of pre-treatment would not be economical. One possible benefit would be the increased VS reduction, and a shorter digestion time. This

could save money by allowing for a smaller digester to be constructed, or perhaps postpone the construction of a new digester if the current digester was near capacity. Theoretically, even if the VSD rate had been increased 2 fold (from 23% to 46%) and biogas was sold at $10.00 GJ total income would amount to an extra $1.40 m^{-3} of sludge treated at 6.5% solids. Estimating disposal costs at $250 Mg^{-1} TS, savings due to sludge pre-treatment would be $3.10 m^{-3}. This is a total savings of $4.50 m^{-3} of sludge treated due to increased biogas production and decreased sludge disposal costs. Muller et al. (2004) estimate that for a municipal wastewater treatment plant theoretically using pre-treatment to improve VSD by 20%, at 5% TS, 250,000 PE sized plant, with much lower pre-treatment energy demand (0.3 kWh $MgTS^{-1}$), pre-treatment would only be economical if sludge disposal costs were greater than $670 Mg^{-1}TS. Specific data for achieved level of disintegration, costs for sludge disposal, and size of wastewater treatment plant must be examined thoroughly to decide if the pre-treatment is worthwhile in each individual setting (Muller et al., 2004).

4.5 Conclusions

- Biogas and methane production (total average of pre-treated and non-treated) from QRP sludge produced 0.51 ± 0.24 and 0.34 ± 0.15 m^3 of biogas $kgVS^{-1}_{consumed}$, respectively.
- Pre-treatment increased volatile solids removal in both the thickened (by 17%) and non-thickened sludge (by 43%).
- Pre-treatment did not increase the overall methane yield, but did increase the initial rate of methane production.

- 80% of total methane/biogas production was reached 5.5-6.5 days faster when pre-treated; therefore reducing the hydraulic retention time.
- Pre-treatment decreased the dewaterability of the sludge.
- Thickening of sludge reduced the total S content of the sludge and subsequently reduced the amount of sulphur liberated during anaerobic digestion.
- Overall, biogas production from pulp sludge was unstable and inconsistent, possibly due to competition between SRB and MPB. Further research is required.

4.6 Acknowledgements

The authors of this paper wish to thank West Fraser, the Quesnel River Pulp Mill, Nick Finch, and Anna Rankin for supplying sludge samples. The City of Prince George helped to supply sludge inoculum samples. Also, we would like to thank Clive Dawson at the British Columbia Ministry of Forests laboratory in Victoria, B.C. for completing some of the analysis. This research was funded by the National Sciences and Engineering Research Council of Canada.

CHAPTER 5: Conclusions and Recommendations

Supermarket fruit and vegetable waste was found to be a relatively clean and reliable source of organic waste. Over 15,000 kg of FVW were co-digested in the anaerobic digester of the Lansdowne Wastewater Treatment Plant over six weeks. Digester operation remained stable, as confirmed by the low total volatile acidity/alkalinity ratio observed; suggesting that more waste could have been added without digester upset. No negative operational consequences were observed downstream from the anaerobic digesters. Co-digestion contributed to an increase in biogas production from the anaerobic digesters. Average daily biogas production during the study period was significantly higher than what was observed historically. Undigested organic matter was found in biosolids produced during the study period suggesting that organic matter should be added to first stage digester in order to prevent "short circuiting" and to increase the hydraulic retention time of the organic waste.

Lab results confirmed that the first stage digester is more favorable over the second for co-digestate addition. First stage digester sludge produced significantly more methane when FVW was added when compared to second stage digester sludge. The increased methane production was most likely due to higher inoculum substrate ratio and increased methanogenic populations in the first stage digester. All of the FVW added was consumed within 10 days suggesting that FVW is an easily digestible source of biodegradable matter for anaerobic digestion.

The high water content of the FVW made the collection and transportation of FVW a limiting factor. Approximately 90% of the FVW was water by mass. The transport of co-digestion substrates with high water content is inefficient. Dewatering of

FVW prior to transportation will improve transportation and handling efficiency as well as the amount of biogas produced per kg of FVW added. More research is needed in this area to improve the economics of the co-digestion of FVW and sewage sludge. Another avenue of research that would benefit the City of Prince George would be the possibility of using other sources of organic waste within the City of Prince George waste stream that are higher in TS than FVW. The organic fraction of municipal solid waste, waste paper, grass clippings, and food waste are all produced within the City of Prince George's operations and could be possible candidates for co-digestion. The large size and low solids content of the digesters allows for significantly higher volumes of co-digestate to be added in the future. Research into the optimum ratios of different types of waste, and changes in seasonal waste variability would be useful for any further full scale studies. Lastly, a longer study period would be useful to highlight any long term consequences of co-digestate addition such as: increased\decreased biosolids output, increased\decreased dewaterability of sludge, foaming and scum, buildup of difficult to degrade components of co-digestate in digesters, increased COD, N, and P output in plant effluent, and downstream mechanical problems due to co-digestate addition.

Overall, addition of organic waste to the first stage anaerobic digester at the Lansdowne wastewater treatment plant is a viable alternative to landfilling for the City of Prince George. The benefits include; increased energy output in the form of biogas, improved sewage sludge digestion, reduced landfill tipping fees, and reduced greenhouse gas emissions.

Combined alkaline and ultrasonic pre-treatment of pulp mill waste activated sludge was shown to also improve anaerobic digestion performance. Pre-treatment

greatly increased the sTS, sVS, and sCOD of both thickened and non-thickened sludge. The increased soluble component of the sludge led to increased rates of methane production. Eighty percent of the total methane was produced 5 - 6 days faster which would significantly reduce the hydraulic retention time in a full scale digester. Over 28 days the effects of pre-treatment diminished and methane production was not significantly greater than without pre-treatment. Pre-treatment of pulp sludge improved the VS reduction, but decreased the sludge dewaterability. Thickening of sludge greatly reduced the amount of sulphur found in the sludge and may be a viable method to reduce the hydrogen sulphide content of the biogas, and prevent possible inhibition. More research is required to directly measure H_2S concentrations in the biogas produced from QRP sludge. Results suggest that SRB may be in competition with MPB causing reduced methane production. If the H_2S concentrations of the biogas were determined it may show that SRB were out competing MPB in the batches with reduced methane production. Optimization of conditions to favor MPB would be useful. More research could also be undertaken to optimize the pre-treatment process on QRP sludge. Sodium hydroxide dosage, reaction time, and ultrasound application should all be tailored to produce maximum soluble COD and minimal cost for the QRP sludge. Optimization would greatly reduce the cost associated with pre-treatment.

The high cost of pre-treatment and the reduction in sludge dewaterability make pre-treatment using ultrasound uneconomical. Other less energy intense pre-treatment methods, such as Microsludge™, or Biogest Crown Disintegration™ may prove to be better methods of pre-treatment. Overall, even with a considerable increase in VS destruction the energy balance may not prove to be worthwhile. Sludge disposal is

relatively cheap at the QRP mill. Pre-treatment has only been shown to be cost effective when sludge disposal costs are high.

Biogas production was unstable and inconsistent from the pulp sludge. A serious problem with the anaerobic digestion of pulp and paper sludge is inhibition. Historically anaerobic digestion was used at the QRP mill, however; due to problems with inconsistent gas production it is no longer used in the wastewater treatment process. Inputs into the pulp mill change depending on the type of pulp produced, species of wood used, and various chemical additives. Methanogenic organisms are very sensitive to environmental changes and react negatively. More research is required to pinpoint potential causes of inhibition at the QRP mill and prevent them. A more thorough investigation into the inhibitory compounds found in the effluent stream is necessary to determine possible causes of toxicity. Experimentation with pilot scale high SRT digesters may prove more resilient to changes in incoming pulp mill wastewater. Often a lack of trace nutrients can cause inhibition during anaerobic digestion. Further research into trace metal concentrations in the QRP effluent may provide further insight into AD optimization.

Lastly, more information about the forms and concentrations of N and P after sludge pre-treatment would be useful to plant operations because pre-treatment could be used to reduce the upstream nutrient dosing requirements for aerobic treatment.

To increase biogas production from pulp sludge co-digestion with an easily degradable substrate would provide more biogas; likely require less energy, and lower initial capital investment than sludge pre-treatment. Co-digestion may also help to dilute

any toxicity found in the pulp mill effluent and improve the final sludge dewaterability. More research in this area is needed.

Literature Cited

AEBIOM. European Biomass Association. A biogas road map for Europe. http://www.aebiom.org/IMG/pdf/Brochure_BiogasRoadmap_WEB.pdf (Accessed July 5 2010)

Ahring, B.K., Ibrahim, A.A., and Mladenovska, Z. 2001. Effect of temperature increase from 55 to 65 °C on performance and microbial population dynamics of an anaerobic reactor treating cattle manure. *Water Research* 35(10):2446-52.

Alatriste-Mondragon, F., Samar, P., Cox, H.J., Ahring, B. Ironpour, R. 2006. Anaerobic codigestion of municipal, farm, and industrial organic wastes: A survey of recent literature. *Water Environment Research* 78(6):607-36.

Alvarez, R., Liden, G., 2008. Semi-continuous co-digestion of solid slaughterhouse waste, manure, and fruit and vegetable waste. *Renewable Energy* 33:726-34.

Altinbas, M., Cifci, D.I., Arikan, O.A., Ozturk, I. 2010. Increasing the biomethane potential of waste activated sludge by food waste under mesophilic and thermophilic conditions, in: *Proceedings Venice 2010, Third International Symposium on Energy from Biomass and Waste* Venice, Italy; 8-11 November 2010.

Amani, T., Nosrati, M., Sreekrishnan. 2010. Anaerobic digestion from the viewpoint of microbiological, chemical, and operational aspects- a review. *Environmental Reviews* 18: 255-78.

American Public Health Association, 1998. Standard Methods for the Examination of Water and Wastewater 1998. 20th ed., American Public Health Association, Washington, DC.

Anhuradha, S., Vijayagopal, V., Radha, P., Ramanujam, R. 2007. Kinetic studies and anaerobic co-digestion of vegetable market waste and sewage sludge. *Clean* 35: 197-99.

Apedaile, E., 2001. A perspective on biosolids management. *Canadian Journal of Infectious Diseases* 12(4):202-04.

Appels, L., Baeyens, J., Degreve, J., Dewil, R. 2008. Principles and potential of the anaerobic digestion of waste-activated sludge. *Progress in Energy and Combustion Science* 34: 755-81.

Balderston, W.L., Payne, W.J. 1976. Inhibition of methanogenesis in salt marsh sediments and whole-cell suspensions of methanogenic bacteria by nitrogen oxides. *Applied Environmental Microbiology* 32:264–69.

Bolzonella, D., Battistoni, P., Susini, C., Cecchi, F. 2006. Anaerobic co-digestion of waste activated sludge and OFMSW: the experiences of Viareggio and Treviso plants (Italy), *Water Science and Technology* 53(8): 203-11.

Bouallagui, H., Touhami, Y., Cheikh, B., Hamdi, M. 2005. Bioreactor performance in anaerobic digestion of fruit and vegetable wastes, *Process Biochemistry* 40(3-4): 989-95.

Bouallagui, H., Lahdheb, H., Ben Romdan, E., Rachdi, B., Hamdi, M. 2009. Improvement of fruit and vegetable waste anaerobic digestion performance and stability with co-substrate addition. *Journal of Environmental Management* 90: 1844-49.

British Columbia Ministry of Environment. 2008. Land application guidelines for the organic matter recycling regulation and soil amendment code of practice. http://www.env.gov.bc.ca/epd/industrial/regs/codes/soil_amend/pdf/land-app-guide-soil-amend.pdf (Accessed 10 December 2010)

Caffaz, S., Bettazzi, E., Scaglione, D., Lubello, C. 2008. An integrated approach in municipal WWTP: anaerobic codigestion of sludge with organic waste and supernatant. *Water Science and Technology* 58(3):669-76.

Canales, A., Pareilleux, A., Rols, J.L., Goma, G., Huyard, A. 1994. Decreased sludge production strategy for domestic wastewater treatment. *Water Science and Technology* 30(8):97-106.

Chae, K.J., Jang, A., Yim, S.K., Kim, I.S. 2008. The effects of digestion temperature and temperature shock on the biogas yields from mesophilic anaerobic digestion of swine manure. *Bioresource Technology* 99(1):1-6.

Chen, Y., Cheng, J., Creamer, K. 2008. Inhibition of Anaerobic digestion process: A review. *Bioresource Technology* 99(10):4044-64.

Chen, X., Rowena, T., Ruihong Zhang, R. 2010. Anaerobic digestion of food wastes for biogas production. *Journal of Agricultural and Biological Engineering* 3(4):1-13.

CH2MHill Canada. 2000. Biosolids Generation, Treatment, Use and Disposal in Canada. Opportunities for Energy Recovery and Greenhouse Gas Reduction Report. Prepared for Environment Canada.

Coackley, P., Jones, B.R.S., 1956. Vacuum Sludge Filtration: 1. Interpretation of results by the concept of specific filtration. *Sewage and Industrial Wastes* 28(8):963-76.

Cogger, C.G., Bary, A.I., Fransen, S.C., Sulivan, D.M. 2001. Seven years of biosolids versus inorganic nitrogen application to tall fescue. *Journal of Environmental Quality* 30(6):2188-94.

Corti, A., Lombardi, L. 2007. Anaerobic co-digestion of source selected organic waste and sewage sludge. *Proceedings Sardinia 2007, Eleventh International Waste Management and Landfill Symposium* S. Margherita di Pula, Cagliari, Italy; 1 - 5 October 2007

Chiu, Y., Chang, C., Lin, J., Huang, S., 1997. Alkaline and ultrasonic pre-treatment of sludge before anaerobic digestion. *Water Science and Technology* 36(11):155-62.

Chu, C.P., Chang, B.V., Liao, G.S., Jean, D.S., Lee, D.J. 2001. Observations on changes in ultrasonically treated waste-activated sludge. *Water Research* 35(4):1038-46.

Chynoweth, D., Isaacson, R. 1987. *Anaerobic Digestion of Biomass.* Elsevier Applied Science, New York.

Daniel, G., Morton, R., Chi-Chung, T., Horvath, R., 2007. The effect of the Microsludge^{TM} treatment process on anaerobic digestion performance. Proceedings of the Water Environment Federation (21-30):1724-38.

Davidsson, A., Gruvberger, C., Christensen, T., Lund Hansen, T., Cour Jansen, J. 2007. Methane yield in source sorted organic fraction of municipal solid waste. *Waste Management* 27(3):406-14.

Delee, W., O'Neill, C., Hawkes, F., Pinhero, H. 1998. Anaerobic Treatment of Textile Effluents: a Review, *Journal of Chemical Technology and Biotechnology* 73(4): 323-35.

Deublein, D., Steinhauser, A. 2008. Biogas from waste and Renewable Resources. Wiley, Wheinheim.

Dietz, W. 1967. Response factors for gas chromatographic analyses. *Journal of Gas Chromatography* 5:68-71.

DiLallo, R., Alberton, O.E. 1961. Volatile acids by direct titration. *Journal Water Pollution Control Federation* 33(4): 356-65.

Dogan, I., Sanin, D.F., 2009. Alkaline solubilisation and microwave irradiation as a combined sludge disintegration and minimization method. *Water Research* 43,(8): 2139-48.

Dufresne, R., Liard, A., Blum, M., 2001. Anaerobic treatment of condensates: trial at a kraft pulp and paper mill. *Water Environment Res*earch 73(1):103-9.

Eastman, J., Ferguson, J. 1981. Solubilization of particulate organic carbon during the acid phase of anaerobic digestion. *Journal Water Pollution Control Federation,* 53(3):352-66.

Edelmann, W., Engell, H., Gradenecker, M. 2000. Co-digestion of organic solid waste and sludge from sewage treatment. *Water Science and Technology* 41(3):213-21.

Elliot, A., Mahmood, T. 2007. Pretreatment technologies for advancing anaerobic digestion of pulp and paper biotreatment residues. *Water Research* 41(19):4273-86.

Environment Canada. 2010. Environmental indicators: Municipal Wastewater Treatment. http://www.ec.gc.ca/indicateurs-indicators/default.asp?lang=En&n=2647AF7D-1 (Accessed Sept 2011)

Forester-Carneiro, T., Perez, M., Romero, L.I. 2008. Influence of total solid and inoculum contents on performance of anaerobic reactors treating food waste. *Bioresource Technology* 99(15):6994-7002.

Froud, C., Weber, R., Schmitt, W., 2005. Collective experience of the crown sludge disintegration system for carbon release for improved biological treatment-final results, in: Proceedings of the 10th European Biosolids and Biowaste Conference, Wakefield, UK.

Garcia, A.I., Gomez, X., Moran, A., Otero, M. 2010. Anaerobic Co-digestion of sewage sludge and organic fraction of municipal solid wastes :different proportions of sludge in the mixture. *Proceedings Venice 2010, Third International Symposium on Energy from Biomass and Waste* Venice, Italy; 8-11 November 2010

Garton, R. 2010. Chief Wastewater Treatment plant operator at the Lansdowne Wastewater Treatment Plant, Prince George, B.C., CA. Personal communication. (10 December 2010)

Gerardi, M. 2003. *The microbiology of anaerobic digesters.* Wiley, New Jersey.

Gooch, M., Felfel, A., Marenick, N. (2010) Food waste in Canada: Opportunities to increase the competitiveness of Canada's agri-food sector, while simultaneously improving the environment. Value Chain Management Centre. http://www.vcmtools.ca/pdf/Food%20Waste%20in%20Canada%20120910.pdf (accessed April 19 2011)

Gomez, X., Cuestos, M.J., Cara, J., Moran, A., Garcia, A.I. 2006. Anaerobic co-digestion of primary sludge and fruit and vegetable fraction of the municipal solid wastes Conditions for mixing and evaluation of the organic loading rate. *Renewable Energy* 31(12):2017-24.

Habiba, L., Hassib, B., Moktar, H. 2009. Improvement of activated sludge stabilization and filterability during anaerobic digestion by fruit and vegetable waste addition. *Bioresource Technology* 100(4): 1555-60.

Hach. Procedure Method 8000, Oxygen demand, chemical, High range. http://www.hach.com/fmmimghach?/CODE%3AOXYGENCOD_NONE_HIGH_2091%7C1 (accessed 12 December 2010)

Haight, M. 2005. Assessing the environmental burdens of anaerobic digestion in comparison to alternative options for managing the biodegradable fraction of municipal solid wastes. *Water Science and Technology* 52(1-2):553-59.

Hamzawi, N., Kennedy, K.J., McLean, D.D. 1998. Anaerobic digestion of co-mingled municipal solid waste and sewage sludge. *Water Science and Technology* 38(2): 127-32.

Heipieper, H.J., Weber, F.J., Sikkema, J., Kewelch, H., de Bont, J.A.M. 1994 Mechanisms of resistance of whole cells to toxic organic solvents. *Trends Biotechnology* 12(10):409–15.

Hendriks, A.T.W.M., Zeeman, G. 2009. Pre-treatments to enhance the digestibility of lignocellulosic biomass. *Bioresource Technology* 100(1):10-9.

Heo, N., Park, S., Kang, H., 2003. Solubilization of waste activated sludge by alkaline pre-treatment and biochemical methane potential (BMP) test for anaerobic co-digestion of municipal organic waste. *Water Science and Technology* 48(8):211-19.

Hogan, F., Mormede, S., Clark, P., Crane, M. 2004. Ultrasound sludge treatment for enhanced anaerobic digestion. *Water Science and Technology* 50(9):25-32.

IEA Task 37- Energy from biogas and Landfill gas Country Report- Canada, April, 2010. http://www.iea-biogas.net/ (Accessed July 5 2010)

IPCC, 2011: Summary for Policymakers. In: IPCC Special Report on Renewable Energy Sources and Climate Change Mitigation [O. Edenhofer, R. Pichs-Madruga, Y. Sokona, K. Seyboth, P. Matschoss, S. Kadner, T. Zwickel, P. Eickemeier, G. Hansen, S. Schlömer, C. von Stechow (eds)], Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

IPCC, 2007: Climate Change 2007: Synthesis report

Iranpour, R., Cox, H.J., Kearney, R.J., Clark, J.H., Pincince, B., Diagger, G.T. 2004. Regulations for biosolids land application in U.S. and European Union. *Journal of Residuals Science & Technology* 1(4):209-14.

Jeihanipour, A., Niklasson, C., Taherzadeh, M. 2011. Enhancement of solubilization rate of cellulose in anaerobic digestion and its drawbacks. *Process Biochemistry* 46(7):1509-14.

Jeyanayagam, S., Eldrige, R., Collins, Jr., 1984. Weed seed survival in a dairy manure anaerobic digester. *Transactions of the ASABE* 27(5):1518-23.

Kalago, Y., Monteith, H. 2008.Water Environment Research Foundation. State of science report: energy and resource recovery from sludge. Global waster research coalition.http://www.iwahq.org/contentsuite/upload/iwa/Document/GWRC_report_Energy and_Resource_Recovery_(2007).pdf (Accessed Sept 20, 2011)

Karlsson, A., Truong, X., Gustavsson, J., Svensson, B., Nilsson, F., Ejlertsson, J. 2011. Anaerobic treatment of activated sludge from Swedish pulp and paper mills-biogas production potential and limitations. *Environmental Technology* 32(14): 1559-71.

Kayhanian, M. 1999. Ammonia inhibition in high solids biogasification- An overview and practical solutions. *Environmental Technology* 20(4):355-65.

Kearney, T., Larkin, M., Frost, J., Levett, P. 1993. Survival of pathogenic bacteria during mesophilic anaerobic digestion of animal waste. *Journal of Applied Bacteriology* 75(3):215-19.

Kepp, U., Machenbach, I., Welsz, N., Solhelm, O. 2000. Enhanced stabilization of sewage sludge through thermal hydrolysis-three years experience with full scale plant. *Water Science and Technology* 42(9):89-96.

Khanal, S. 2008. *Anaerobic Biotechnology for Bioenergy Production.* Wiley-Blackwell, Ames, USA.

Khanal, S.K., Grewell, D., Sung, S., van Leeuwen, J. 2007. Ultrasound applications in wastewater sludge pre-treatment: A review. *Critical Reviews in Environmental Science and Technology* 37(4):277-313.

Khanal, S.K., Isik, H., Sung, S., van Leeuwen, J. 2006. Effects of ultrasound pre-treatment on aerobic digestibility of thickened waste activated sludge. Proceedings of 7th specialized conference on small water and wastewater systems, March 7-10, Mexico City, Mexico.

Kim H.W., Han, S. K., Shin, H. S., 2003. The optimisation of food waste addition as a co- substrate in anaerobic digestion of sewage sludge. *Waste Management and Research* 21(6):515-26.

Kim, J., Park, C., Kim, T., Lee, M., Kim, S., Lee, J., 2003. Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge. *Journal of Bioscience and Bioengineering* 95(3):271-75.

Kubler, H., Hoppenheidt, K., Hirsch, P., Kottmair, A., Nimmrichter, R., Nordsieck, H.,

Mucke, W., Swerev, M. 2008. Full scale co-digestion of organic waste. *Water Science and Technology* 41(3):195-202.

Kyllonen, H.L., Lappi, M.K., Thun, R.T., Musteanta, A.H. 1988. Treatment and characterisation of biological sludges from the pulp and paper industry. *Water Science Technology* 20(1):183-92.

U.S. Energy Information Administration (IEA). 2010. World energy demand and economic outlook. http://205.254.135.24/oiaf/ieo/world.html (Accessed September 2011)

Lettinga, G., Rebac, S., Zeeman, G. 2001. Challenge of psychrophilic anaerobic wastewater treatment. *Trends in Biotechnology* 19(9):363-71.

Lin, J., Zuo, J., Wang, K., Liu, F. 2010. Bioenergy recovery from fruit and vegetable waste by anaerobic digestion. *Proceedings Venice 2010, Third International Symposium on Energy from Biomass and Waste* Venice, Italy; 8-11 November 2010

Lin, Y., Wang, D., Li, Q., Xiao, M. 2011. Mesophilic batch anaerobic co-digestion of pulp and paper sludge and monosodium glutamate waste liquor for methane production in a bench scale digester. *Bioresource Technology* 102(4):3673-78.

Lin, Y., Wang, D., Wu, S., Wang, C. 2010. Biological pretreatment enhances biogas production in the anaerobic digestion of pulp and paper sludge. *Waste Management Research* 28(1):800-10.

Lin, Y., Wang, D., Wu, S., Wang, C. 2009. Alkali pretreatment enhances biogas production in the anaerobic digestion of pulp and paper sludge. *Journal of Hazardous Materials* 170(1):366-73.

Liu, G., Zhang, R., El-Mashad, H., Dong, R. 2009. Effect of feed to inoculum ratios on biogas yields of food and green wastes. *Bioresource Technology* 100(21):5103-08.

Mahmood, T., Elliot, A. 2006. A review of secondary sludge reduction technologies for the pulp and paper industry. *Water Research* 40(11):2093-112.

Mao, T., Hong, S.Y., Show, K.Y., Tay, J.H., Lee, D.J. 2004. A comparison of ultrasound treatment on primary and secondary sludges. *Water Science and Technology* 50(9):91-97.

Marche, T., Schnitzer, M., Dinel, H., Pare, T., Champagne, P., Schultenc, H.R., Facey, G. 2003. Chemical changes during composting of a paper mill sludge-hardwood sawdust mixture. *Geoderma* 116(3-4):345-6.

Mata-Alverez, J., Mace, S., Llabres, P. 2000. Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives. *Bioresource Technology* 74(1):3-16.

Mata-Alvarez, J., Dosta, J., Mace, S., Astals, S. 2011. Codigestion of solid wastes: A review of its uses and perspectives including modeling. *Critical Reviews in Biotechnology* 31(2):99-111.

Muller, J.A., Winter, A., Strunkmann, G. 2004. Investigation and assessment of sludge pre-treatment processes. Water Science and Technology 49(10):97-104.

Muradov, N., Veziroglu, T. 2008. "Green" path from fossil-based to hydrogen economy: An overview of carbon-neutral technologies. *International Journal of Hydrogen Energy* 33(23):6804-39.

Murto, M., Bjornsson, L., Mattiasson, B. 2004. Impact of food industrial waste on anaerobic co-digestion of sewage sludge and pig manure. *Journal of Environmental Management* 70(2):101-7.

McCarty, P.L. 2001. The development of anaerobic treatment and its future. *Water Science and Technology* 44(8):149-56.

McCarty, P.L. 1964. Anaerobic Waste Treatment Fundamentals. Part One: Chemistry and Microbiology. *Public Works* 107-10.

Mohan, S., Bindhu, B.K. 2008. Effect of phase separation on anaerobic digestion of kitchen waste. *Journal of Environmental Engineering and Science* 7(2):91-103.

Moigno, A. F. 1882. Mouras' Automatic Scavenger. *Minutes of the proceedings of the Institution of Civil Engineers.*

Nallathambi Gunaseelan, V. 2004. Biochemical methane potential of fruits and vegetable solid waste feedstocks. *Biomass and Bioenergy* 26(4):389-99.

Navia, R., Soto, M., Vidal, G., Bornhardt, C., Diez, M.C. 2002. Alkaline pretreatment of Kraft mill sludge to improve its anaerobic digestion. *Bulletin of Environmental Contamination and Toxicology* 69(6):869-76.

Nazareth, V., Kuzyk, R., Szoke, N., Oka, K., Barsalou, P., Wilson, S. 2003. Tale of Two Cities – Toronto and Winnipeg: Public Participation in Biosolids Planning, 2 nd Canadian Organic Residuals Recycling Conference, Penticton.

Neves, L. Oliveira, R. Alves, M. 2009. Co-digestion of cow manure, food waste and intermittent input of fat. *Bioresource Technology* 100(6):1957-62.

Neyens, E., Baeyens, J., 2003. A review of thermal sludge pre-treatment processes to improve dewaterability. *Journal of Hazardous Materials* 98(1-3):51-67.

Noike, T., Endo, G., Chang, J., Yagucchi, J., Matsumoto, J. 1985. Characteristics of carbohydrate degradation and the rate-limiting step in anaerobic digestion. *Biotechnology and Bioengineering* 27(10):1482-89.

Novaes, R.F.V. 1986. Microbiology of Anaerobic Digestion. *Water Science and Technology* 18(12):1-14.

Operation of municipal wastewater treatment plants; Volume 1: Management and support systems 2008. 6th ed. Water Environment Federation, USA.

Park, N., Thring, R.W, Garton, R., Rutherford, M., Helle, S. 2011. Increased biogas production in a wastewater treatment plant by anaerobic co-digestion of fruit and vegetable waste and sewer sludge- A full scale study. *Water Science and Technology* 64(9):1851-6.

Parkarinen, O., Bayr, S., Paavola, T., Mantyla, E., Kaparaju, P., Rintala, J. 2010. Methane and hydrogen production of pulp and paper industry primary sludges. *Proceedings Venice 2010, Third International Symposium on Energy from Biomass and Waste* Venice, Italy; 8-11 November 2010.

Pilli, S., Bhunia, P., Yan, S., LeBlanc, R.J., Tyagi, R.D., Surampalli, R.Y. 2011. Ultrasonic pretreatment of sludge: A review. *Ultrasonics Sonochemistry* 18(1):1-18.

Prescott, C.E., Belvins, L.L. 2005. Eleven-year growth response of young conifers to biosolids or nitrogen and phosphorous fertilizer on northern Vancouver Island. *Canadian Journal of Forest Research* 35(1):211-14.

Raposo, F., Borja, R., Martin, M.A., Martin, A., del la Runia, M.A., Rincon, B. 2009. Influence of inoculum–substrate ratio on the anaerobic digestion of sunflower oil cake in batch mode: Process stability and kinetic evaluation. *Chemical Engineering Journal* 149(1-3):70-77.

Puhakka, J., Alavakeri, M., Shieh, W. 1992. Anaerobic treatment of Kraft pulp-mill waste activated-sludge: Gas production and solids reduction. *Bioresource Technology* 39(1):61-68.

Reardon, D.J. 1995. Turning down the power. *Civil Engineering* 65(8):54-6.

Rinzema, A., Boone, M., van Knippenberg, K., Lettinga, G. 1994. Bactericidal effect of long chain fatty acids in anaerobic digestion. *Water Environment Research* 66(1): 40–9.

Rizk, M.C., Bergamasco, R., Granhen Tavares, C. R. 2007. Anaerobic co-digestion of fruit and vegetable waste and sewage sludge. *International Journal of Chemical Reactor Engineering* 5 A29.

Rulkens, W.H. 2004. Sustainable sludge management- what are the challenges for the future? *Water Science and Technology* 49(10):141-9.

Saev, M., Koumanova, B., Simeonov, I. 2009. Anaerobic Co-digestion of wasted vegetables and activated sludge. *Biotechnology and Biotechnological Equipment* 23: 832- 835.

Saha, M., Eskicioglu, C., Marin, J. 2011. Microwave, ultrasonic and chemo-mechanical pretreatments for enhancing methane potential of pulp mill wastewater treatment sludge. *Bioresource Technology* 102(17):7815-26.

Santos, H.M., Lodeiro, C., Capelo-Martinez, J.L. 2009. The Power of Ultrasound. In: *Ultrasound in Chemistry: Analytical Applications.* Wiley, Weinheim.

Sawyer, C., McCarty, P., Parkin, G. 2003. Chemistry for environmental engineering science, 5th ed. McGraw-Hill, Inc. New York, USA.

Scaglione, D., Caffaz, S., Ficara, E., Malpei, F., Lubello, C. 2008. A simple method to evaluate the short-term biogas yield in anaerobic co-digestion of WAS and organic wastes. *Water Science and Technology* 58(8):1615-22.

Shimizu, T., Kudo, K., Nasu, Y. 2004. Anaerobic waste-activated sludge digestion-a bioconversion mechanism and kinetic model. *Biotechnology and Bioengineering,* 41(11):1082-91.

Shizas, I., Bagley, D.M. 2004. Experimental determination of energy content of unknown organics in municipal wastewater streams. *Journal of Energy Engineering* 130(2): 45-53.

Show, Y.K., Mao, T., Lee, D.J. 2007. Optimization of sludge disruption by sonication. *Water Research* 41(20):4741-47.

Siddiqui, Z., Horan, N.J., Anaman, K. 2011. Optimisation of C :N ratio for co-digested processed industrial food waste and sewage sludge using the BMP test. *International Journal of Chemical Reactor Engineering* 8 S4.

Sievers, M., Reid, A., Knoll, R. 2004. Sludge treatment by ozonation-evaluation of full scale results. *Water Science and Technology* 49(4):247-53.

Sikkema, J., De Bont, J., Poolman, B. 1995. Mechanisms of membrane toxicity of hydrocarbons. *Microbiological Reviews* 59(2):201–22.

Sinclair, W.F. 1990 Controlling pollution from Canadian pulp and paper manufactures: a federal perspective, Canadian Government Publishing Centre, Ottawa.

Singh, R.P., Agrawal, M. 2008. Potential benefits and risks of land application of sewage sludge. *Waste Management* 28(2):347-58.

Singh, R.P., Kumar, S., Ojha, C.S.P. 1999. Nutrient requirement for UASB process: a review. *Biochemical Engineering Journal* 3(1):35-54.

Smith, S., Lang, N., Cheung, K., Spanoudaki, K. 2005. Factors controlling pathogen destruction during anaerobic digestion of biowastes. *Waste Management* 25(4): 417-25.

Sonotronic Technologies. Sonication of Biosolids. http://www.sonotronic.de/technologies/ultrasonic/sonication-of-bio-solids?set_language=en (Accessed October, 2011)

Sosnowski, P., Wieczorek, A., Ledakowicz, S. 2003. Anaerobic co-digestion of sewage sludge and organic fraction of municipal solid wastes. *Advances in Environmental Research* 7(3):609-16.

Sosnowski, P., Klepacz-Smolka, A., Kaczorek, K. Ledakowicz, S. 2008. Kinetic investigations of methane co-fermentation of sewage sludge and organic fraction of municipal solid wastes. *Bioresource Technology* 99(13):5731-37.

Statistics Canada, 2007. Industrial Water Use. http://www.statcan.gc.ca/pub/16-401-x/16-401-x2010001-eng.pdf (Accessed September 2011)

Statistics Canada. 2008a. Human activity and the environment: Food in Canada. http://www.statcan.gc.ca/daily-quotidien/090609/dq090609a-eng.htm (Accessed September 2011)

Statistics Canada. 2008b. Study: Composting organic waste. http://www.statcan.gc.ca/daily-quotidien/080327/dq080327c-eng.htm (Accessed December 2010)

Statistics Canada. Human activity and the environment: Food in Canada. 2009. http://www.statcan.gc.ca/daily-quotidien/090609/dq090609a-eng.htm (Accessed September 2010)

Stepan, D. The breakdown on anaerobic digestion. *Biomass Magazine.* June 2008. http://www.biomassmagazine.com/article.jsp?article_id=1680 (Accessed July 2010)

Stephanson, R., Rabinowitz, B., Laliberte, S., Elson, P., 2005. Teaching an old digester

new tricks: full scale demonstration of the Microsludge process to liquefy municipal waste activated sludge, in: WEF Proceedings of the Residuals and Biosolids Management Conference, Covington, KY.

Stickley, D.P. 1970. The effect of chloroform in sewage on the production of gas from laboratory digesters. *Water Pollution Control* 69:585–90.

Stroot, P.G., McMahon, K.D., Mackie, R.I., Raskin, L. 2001. Anaerobic co-digestion of municipal solid waste and biosolids under various mixing conditions-I. digester performance. *Water Research* 35(7):1804-16.

Thompson, G., Swain, J., Kay, M., Forster, C.F. 2001. The treatment of pulp and paper mill effluent: a review. *Bioresource Technology* 77(3):275-86.

Vallee, B.L., Ulner, D.D. 1972. Biochemical effects of mercury, cadmium, and lead. *Annual Review of Biochemistry* 41:91–128.

Wang, F., Shan, L., Ji, M. 2006. Components of released liquid from ultrasonic waste activated sludge disintegration. *Ultrasonic Sonochemistry* 13(4):334-38.

Wang, F., Wang, Y., Ji, M., 2005. Mechanisms and kinetic models for ultrasonic waste activated sludge disintegration. *Journal of Hazardous Materials*, 123(1-3):145-150

Ward, A., Hobbs, P., Holliman, P., Jones, D. (2008). Optimization of the anaerobic digestion of agricultural resources. *Bioresource Technology* 99(17):7928-40.

Wood, N., Tran, H., Master, E. 2009. Pretreatment of pulp mill secondary sludge for high- rate anaerobic conversion to biogas. *Bioresource Technology* 100(23):5729-35.

Yen, H.W., Brune, D. E. 2007. Anaerobic co-digestion of algal sludge and waste paper to produce methane. *Bioresource Technology* 98(1):130-4.

Yiying, J.I.N., Huan, L.I. 2009. Combined alkaline and ultrasonic pre-treatment of sludge before anaerobic digestion. *Journal of Environmental Sciences* 21(3):279-84.

Yoneyama, Y., Takeno, K. 2002. Co-digestion of domestic kitchen waste and night soil sludge in a full-scale sludge treatment plant. *Water Science and Technology* 45 (10):281-86.

Zhang, R., El-Mashad, H., Hartman, K., Wang, F., Lui, G., Choate, C., Gamble, P., 2007. Characterization of food waste as feedstock for anaerobic digestion. *Bioresource Technology* 98(4):929-35.

Zitomer, D., Adhikari, P., 2005. Extra methane production from municipal anaerobic digesters. *Biocycle* September 64-6.

Zitomer, D.H., Adhikari, P., Heisel, C., Dineen, D. 2008. Municipal anaerobic digester for codigestion, energy recovery, and greenhouse gas reductions. *Water Environment Research* 80(3):229-37.

Zupancic, G., Uranjek-Zevart, N., Ros, M. 2008. Full-scale anaerobic co-digestion of organic waste and municipal sludge. *Biomass and Bioenergy* 32(2):162-7.

Appendix A- Sample calculations

The following sample calculations were performed with data from 10:00 AM, November 12, 2010 (primary digester sludge control, replicate # 1).

Correction of Gas Volume to STP (0°C and 1 atm)

The temperature of the biogas in the bottle headspace was determined to be 31 °C by inserting a thermometer through the septum.

Atmospheric pressure was determined by the University of Northern British Columbia atmospheric sciences roof top weather station located 7 m above the research lab building roof. Data can be found a, "http://cirrus.unbc.ca/wx/".

14 mL of Biogas were collected. Following from the equation,

$$PV = nRT$$

$$\frac{PV}{nRT} = \frac{PV}{nRT}$$

1 (atm) = 101.325 (kPa)

$$\frac{101.325(kPa) \times V(mL)}{nR \times 273.15(K)} = \frac{92.900(kPa) \times 14(mL)}{nR \times 304.15(K)}$$

V= 11.5 (mL)

Correction of Gas Chromatography Response (Peak Areas) for differences in TCD responses between methane and carbon dioxide.

Dietz (1962) published a series of correction factors to compensate for the differences in thermal conductivities between different compounds. These correction factors are specific to thermal conductivity detectors and independent of column type, oven temperature, carrier gas, flow rate, and concentration. They have a precision of approximately ± 3%.

The peak areas must be divided by the appropriate correction factor to obtain the true peak area,

(Peak Area) / (Thermal Response Factor) = Corrected Peak Area

For Methane

33.368 / 35.7 = 0.9347

For Carbon Dioxide

27.812 / 48 = 0.5794

Once the peak areas have been corrected for differences in TCD response the percent volume of the gas can be determined by normalization. It is assumed that the concentrations of trace gases found in the biogas are very low. The presence of trace gases will lower the overall methane and carbon dioxide concentration.

Normalization of Corrected Peak Areas to Calculate Methane Gas Volume in Percent

% Volume CH_4 = [(Corrected Peak Area for CH_4) / (Corrected Peak Area for CH_4) + (Corrected Peak Area for CO_2)] x 100 %

$$= \frac{0.9347}{0.9347 + 0.5794}$$

= 0.6173 x 100 %

= 61.7 % CH_4 by volume

Normalization of Corrected Peak Areas to Calculate Carbon Dioxide Gas Volume in Percent

% Volume CO_2 = [(Corrected Peak Area for CO_2) / (Corrected Peak Area for CH_4) + (Corrected Peak Area for CO_2)] x 100 %

$$= \frac{0.5794}{0.9347 + 0.5794}$$

= 0.3827 x 100 %

= 38.3 % CO_2 by volume

Determination of Volume of Methane in Biogas Samples

$$\text{Volume of } CH_4 = \frac{\text{Percent volume of } CH_4}{100\ \%} \times (\text{Corrected Volume of Biogas})$$

= (0.6173) x (11.5 mL)

= 7.1 mL of CH_4 (at 0 °C and 1 atm)

Determination of ultrasound specific energy (Es) in kJ kg^{-1} TS^{-1} for 2.4% TS sludge

$$Es = \frac{P \times t}{V \times TS}$$

Where, P = ultrasonic power (W), t = ultrasonic time (s), v = sample volume (L), TS = total solids concentration (kg/L).

150W maximum output at 60% amplitude is 90W

$$Es = \frac{90(J/s) \times 4800(s)}{0.4(L) \times 0.0273(kgTS/L)}$$

$$Es = 39560(kJ/kgTS)$$

Calculation of cost of ultrasound pre-treatment for 2.4% TS sludge

Cost = 39560 kJ/kgTS x 27 kgTS/m^3

Cost = (1068120 kJ/m^3) / 4800 s

Cost = 223 kW/m^3 x 1.333 h

Cost = 297 kWh/m^3 x $0.07 per kWh

Cost = $21/$m^3$

Calculation of cost of NaOH addition for 2.4% TS sludge

Dosage of NaOH = 20.6 g NaOH / 100g TS

$$\frac{20.6(gNaOH)}{100(gTS)} = \frac{x(gNaOH)}{24200(gTS/m^3)}$$

Dosage of NaOH = 5 kg NaOH / m^3

$$\frac{\$350}{1000(kgNaOH)} = \frac{\$x}{5(kgNaOH)}$$

Cost of NaOH = $1.75 / m^3

Total pre-treatment cost per m^3 = Cost of ultrasound + Cost of NaOH

Total pre-treatment cost per m^3 = $21 + $1.75

Total cost per m^3 = $22.75

Determination of specific resistance to filtration

Specific resistance to filtration (R) was determined using a plot of filtration time/filtrate volume (t/V) vs. filtrate volume (V).

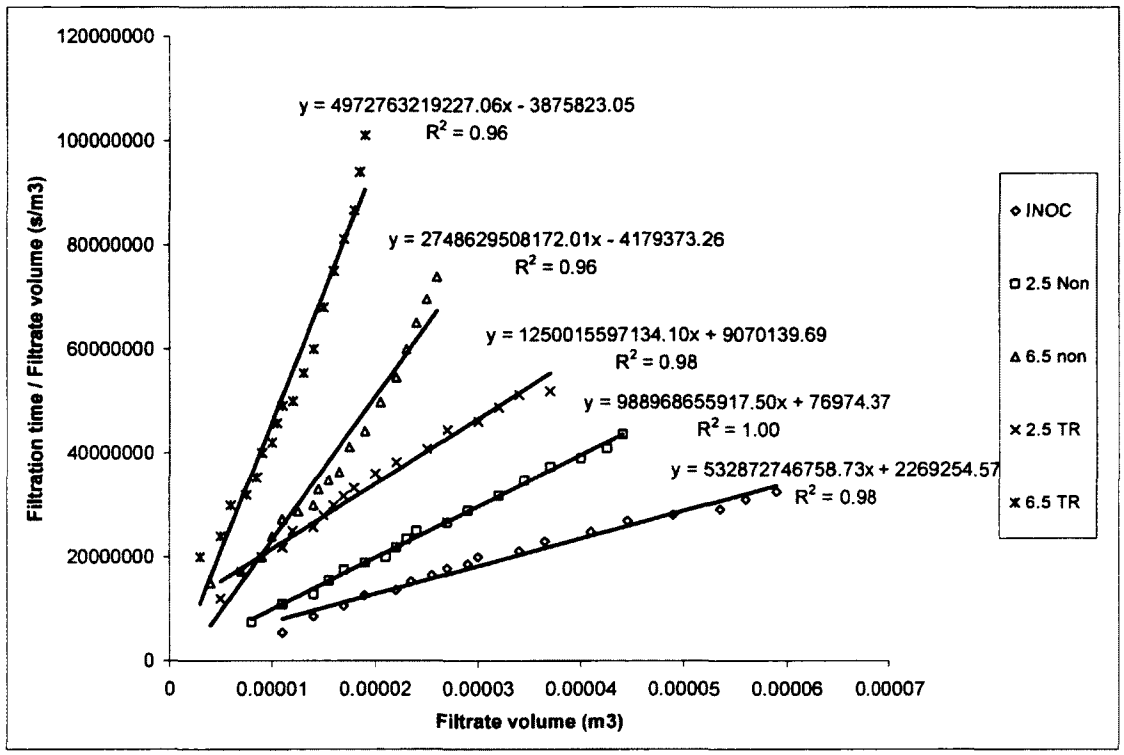

Figure A Plot of filtration time/filtrate volume (t/V) vs. filtrate volume (V) for inoculum, 2.5% TS non-treated, 2.5%TS pre-treated, 6.5%TS non-treated, 6.5%TS pre-treated pulp mill sludge post anaerobic digestion.

Using the slope of the line, R was calculated using the following equation,

$t/V = (\mu Rw/2A^2P)V + \mu Rm/AP$

Where,

"R" is specific resistance to filtration (m kg^{-1})
"P" is the pressure of filtration (bar)
"μ" is the viscosity of the filtrate (Pa s)
"V" is the volume of the filtrate (m^3)
"t" is the filtration time (s)
"w" is the weight of the dry solids per volume of filtrate (kg m^{-3})
"A" is the area of the filter paper (m^2)
"Rm" is the resistance on the medium (m^{-1})

"Rm" is very small for compressible sludge and can be ignored. Therefore the equation is reduced to,

$t\backslash V = (\mu Rw/2A^2P)V$

Using the slope (b) of lines of best fit from Figure A,

$R = (2A^2P/\mu w)b$

For 6.5% TS pre-treated it follows,

$R = [(2 \times (0.00950\ m^2)^2 \times 69000\ Pa) / (0.001307\ Pa\ s \times 32.4\ kg\ m^{-3})] \times 4.9x10^{12}\ (s\ m^{-6})$

$R = [12.45\ m^4\ Pa / 0.0423\ Pa\ s\ kg\ m^{-3}] \times 4.9x10^{12}\ (s\ m^{-6})$

$R = [294.3\ m^7\ s^{-1}\ kg^{-1}] \times 4.9x10^{12}\ (s\ m^{-6})$

$R = 14.6x10^{14}\ m\ kg^{-1}$

Determination of estimated H_2S concentration of biogas

Pre-treated 6.5%:

Total initial S content of dried 6.5% TS sludge = 1.366 ± 0.018%

TS 6.5% (g/batch) = (6.52%/100) x 75 g/batch
= 4.890 ± 0.01 (g/batch)

Standard deviation = (0.013%/100) x 75 g/batch
= 0.01 g/batch

S (g/batch) = (1.366%/100) x 4.890 g/batch
= 0.067 ± 0.001 g/batch

Standard deviation = $\sigma z = z\sqrt{(\frac{\sigma x}{x})^2 + (\frac{\sigma y}{y})^2}$

$$\sigma z = 0.0668\sqrt{(\frac{0.01}{4.890})^2 + (\frac{0.018}{1.366})^2}$$

= 0.001 g/batch

Total S content of dried inoculum = 0.986 ± 0.022%

TS inoculum (g/batch) = (1.67%/100)*75 g/batch

	= 1.2525 ± 0.019 g/batch
S (g/batch)	= (0.986%/100) x 1.2525 g/batch = 0.0123 ± 0.0003 g/batch
Total initial S per batch	= S 6.5% TS sludge + S inoculum = 79.1 ± 1.0 mg/ batch
Final S per batch	= 68.77 mg/ batch
S lost during digestion	= Initial S – Final S = 79.1 – 68.77 = 8.91 ± 1.32 mg/ batch
Net Biogas produced	= 0.549 ± 0.153 L
Concentration of S in gas	= mg S lost / L of biogas produced = 8.91 (mg/batch) / 0.549 (L Biogas/ batch) = (16.23 ± 5.1 mg/L) x 1000 L/ m^3 = 16233 ± 5121 mg/m^3
Concentration of H_2S	= [16233 (mg/ m^3) x 22.4 (L/mol)]/ 34 g/mol = (10694 ± 3374 ppm) /10,000 (ppm/1%vol) = 1.07 ± 0.34 % vol H_2S

Appendix B- Sample chromatograms.

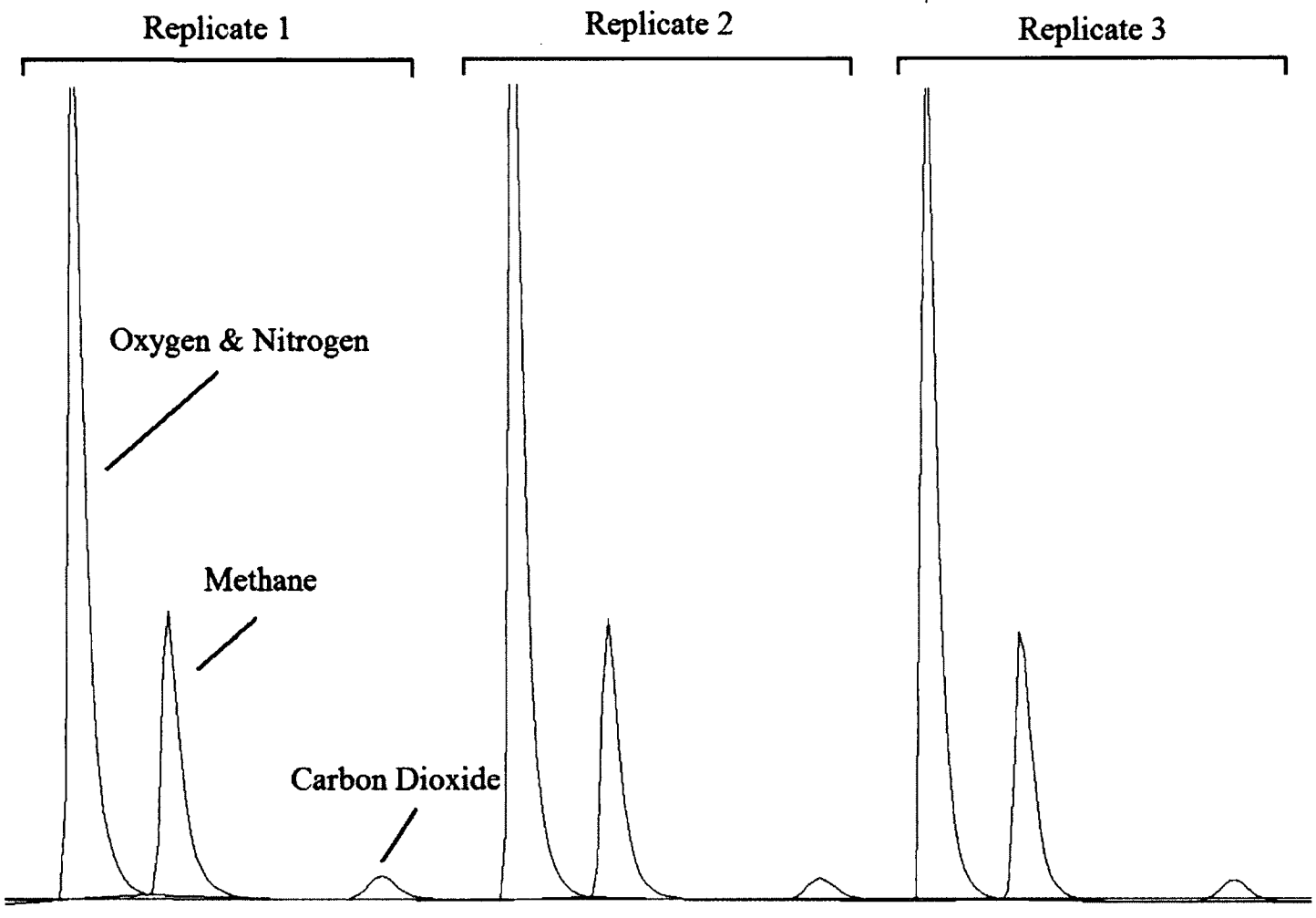

Figure B1- Chromatogram of methane standard and human breath. Gas chromatography conditions are reported in section 4.3.6.

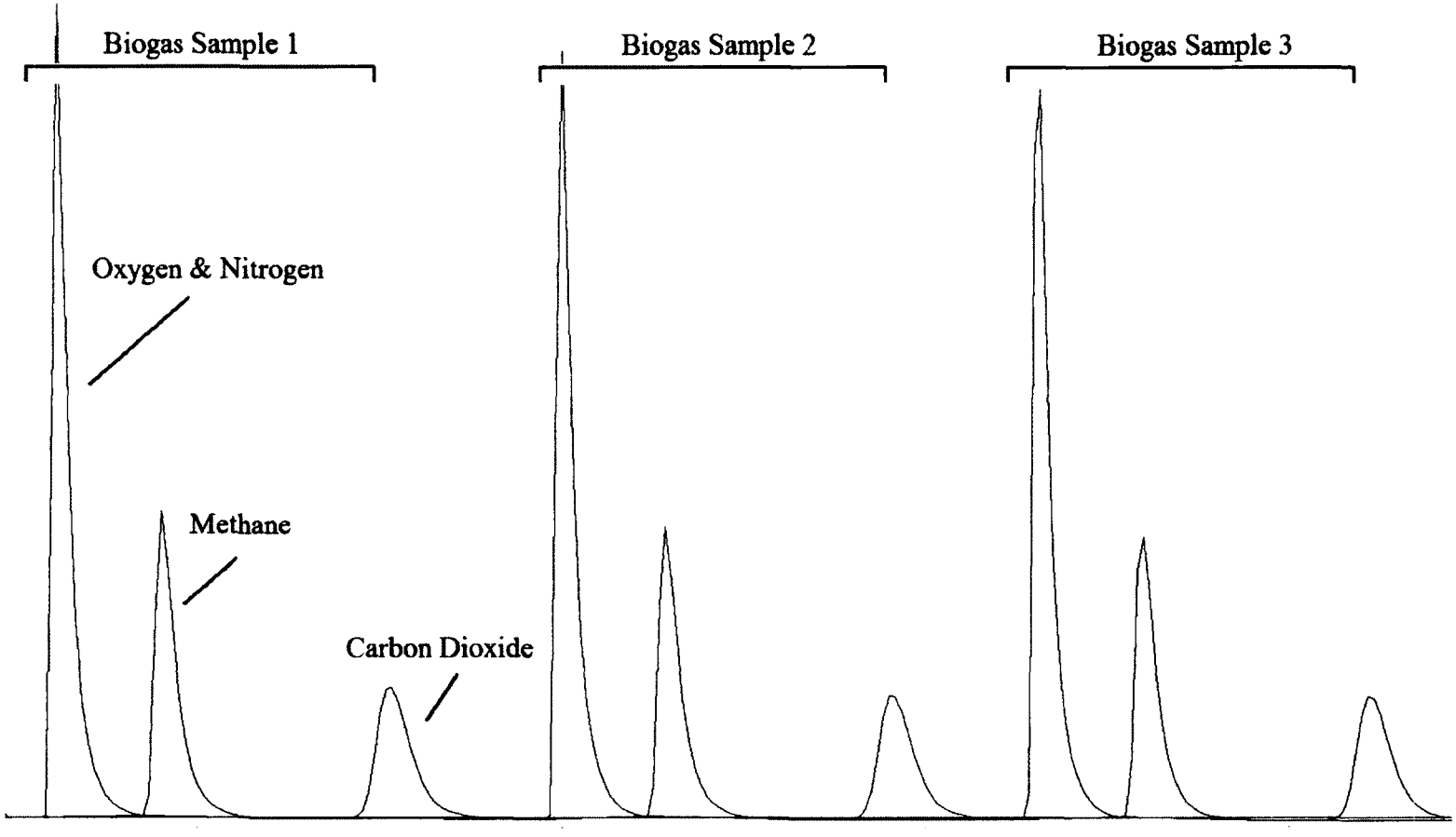

Figure B2- Chromatogram of biogas. Inoculum replicates 1, 2 and 3, 9:00 am, June 19th, 2011. Gas chromatography conditions are reported in section 4.3.6.

Appendix C- Chapter four methane generation raw data

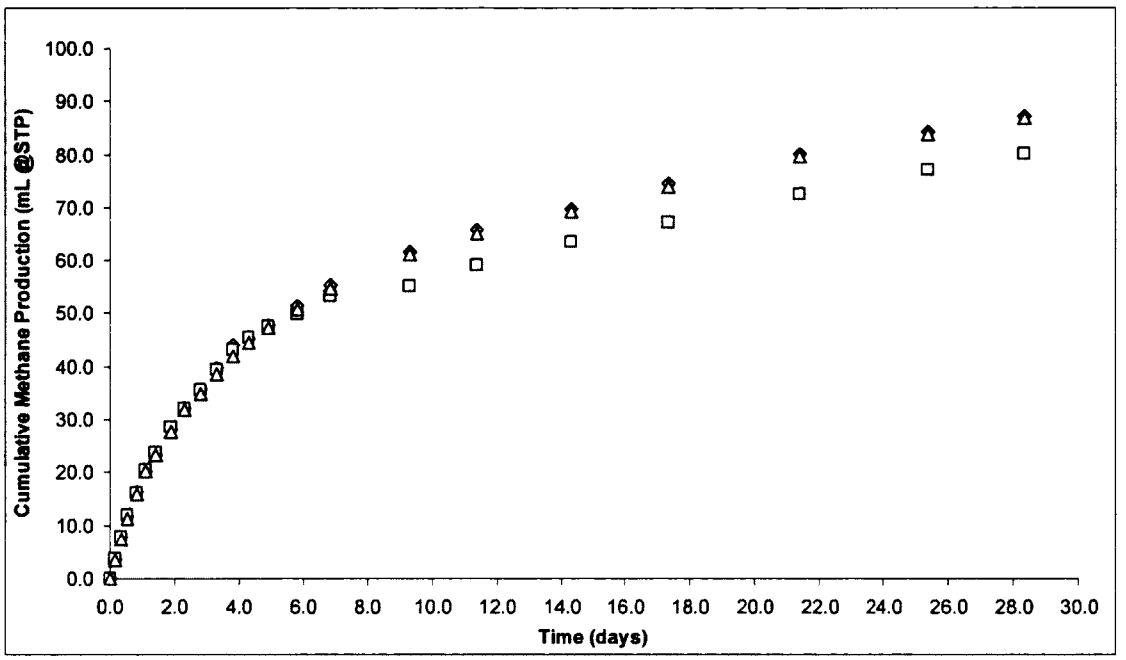

Figure C1 Cumulative methane generation for inoculum at standard temperature and pressure. Δ Replicate 1. □ Replicate 2. ◊ Replicate 3.

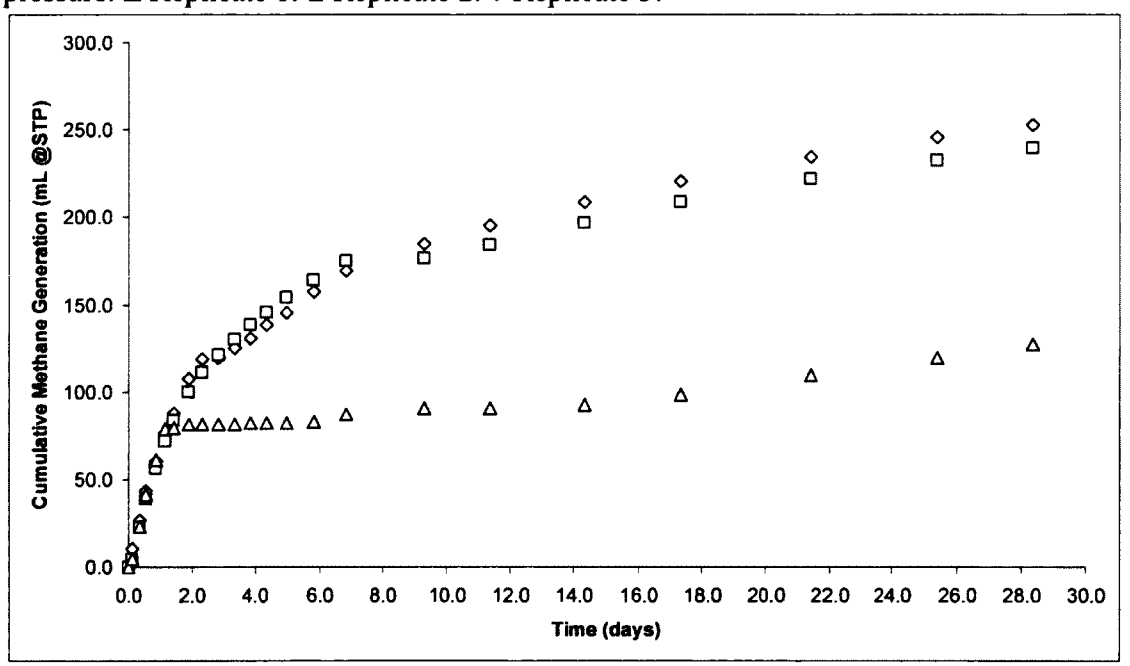

Figure C2 Cumulative methane generation for 2.5%TS, not pre-treated, at standard temperature and pressure. Δ Replicate 1. □ Replicate 2. ◊ Replicate 3.

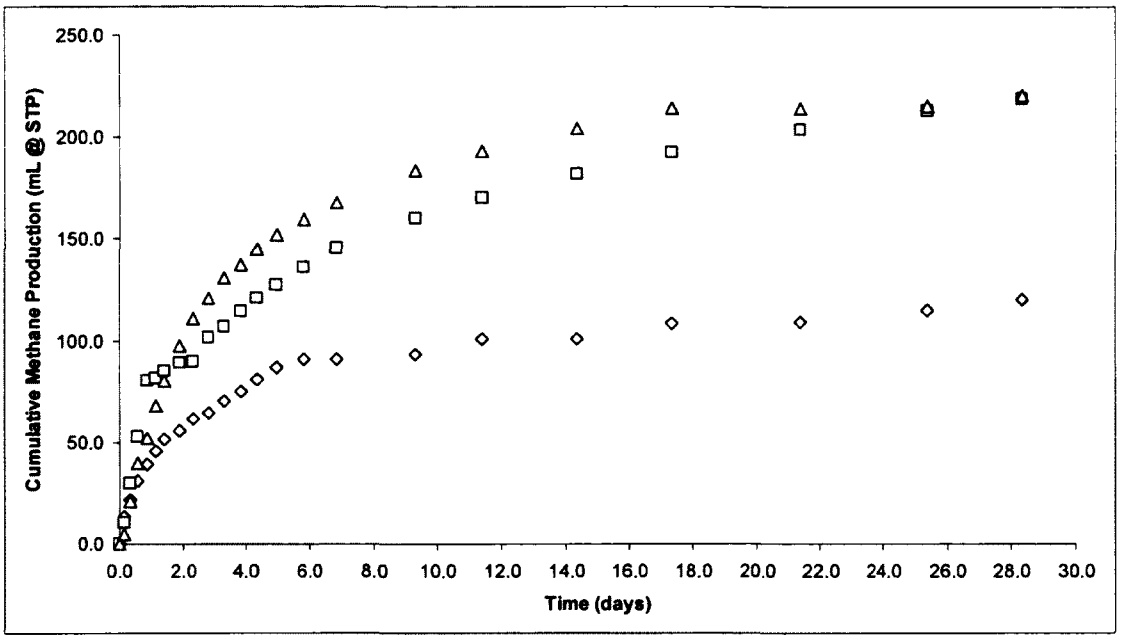

Figure C3 Cumulative methane generation for 2.5%TS, pre-treated, at standard temperature and pressure. Δ Replicate 1. □ Replicate 2. ◊ Replicate 3.

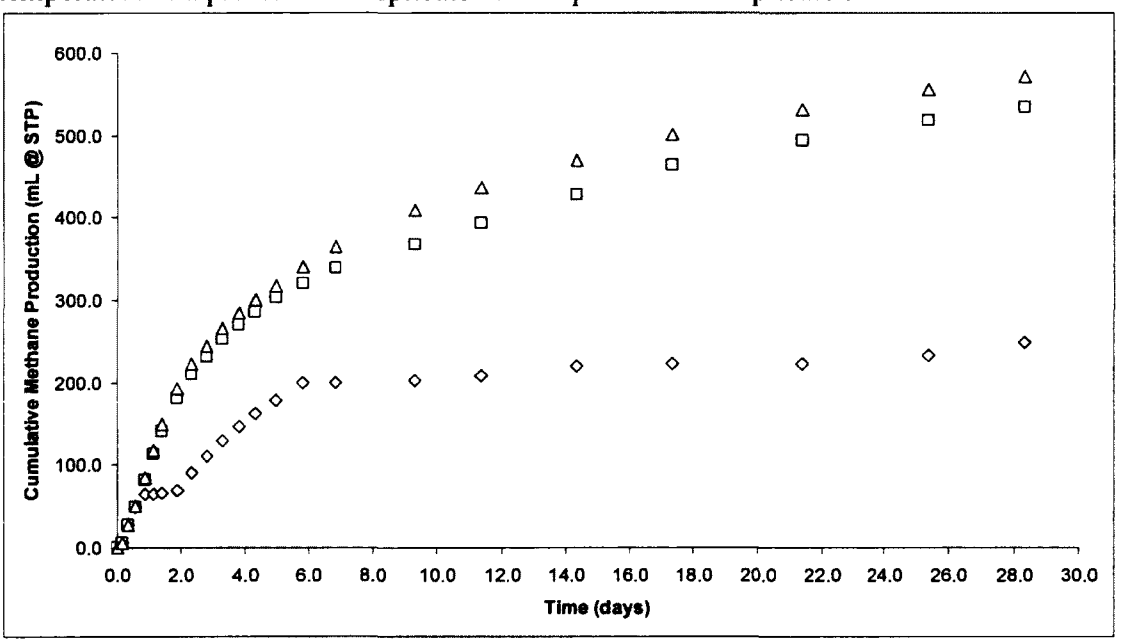

Figure C4 Cumulative methane generation for 6.5%TS, not pre-treated, at standard temperature and pressure. Δ Replicate 1. □ Replicate 2. ◊ Replicate 3.

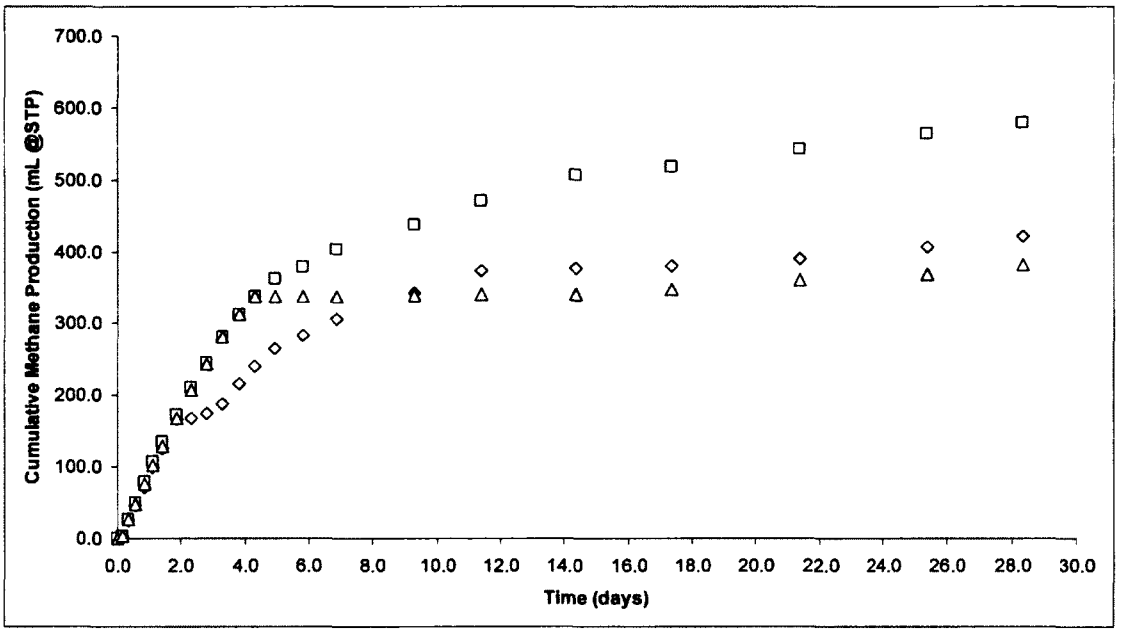

Figure C5 Cumulative methane generation for 6.5%TS, pre-treated, at standard temperature and pressure. Δ Replicate 1. □ Replicate 2. ◊ Replicate 3.